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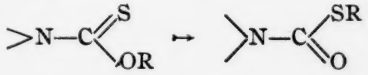
ON THE MOLECULAR REARRANGEMENT OF UNSYMMETRICAL ACYLAMIDINES INTO ISOMERIC SYMMETRICAL DERIVATIVES.

BY HENRY L. WHEELER, TREAT B. JOHNSON, AND DAVID F. MCFARLAND.

In papers from this laboratory, which were published several years ago,[1] it was shown that thioncarbamic esters undergo a molecular rearrangement into thiolcarbamic esters when heated with alkyl halides.

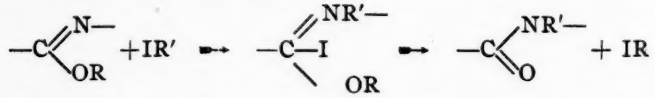


The more negative the radicals attached to nitrogen the less readily the rearrangement took place. Methyl iodide produced a rearrangement more readily than other halides. In the case of the acetylthioncarbamic esters only the methyl derivatives were found to undergo a molecular rearrangement.

It was shown that the aromatic imido esters, in general, readily undergo an analogous metastatic change,[2] while Dr. H. F. Mer-

[1] *Am. Chem. J.*, **22**, 140 (1899); *Ibid.*, **24**, 60, 189, 424 (1900).
[2] *Ibid.*, **21**, 185 (1899); *Ibid.*, **23**, 135 (1900).

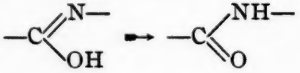
riam has found that the aliphatic members do not show a similar tendency. These molecular rearrangements were brought about catalytically with only a trace of alkyl halide, and here again methyl iodide acted the most readily. By employing a halide with a group different from R, it was shown that the change involved an addition of alkyl to nitrogen and then a separation from oxygen. This may be represented as follows:

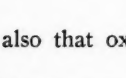
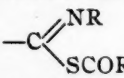


The mechanism of the rearrangement of the thioncarbamic esters was previously shown by us to be similar.

Wislicenus and Goldschmidt[1] found that N-substituted imidoesters undergo a molecular rearrangement on simply heating alone to a high temperature, the imidoesters of Pinner being decomposed by this treatment.

We[2] have found that when R in the above formula is an acyl group, the rearrangement takes place by heat alone far more readily than when it is an alkyl group. In fact, some of these acyl derivatives (acyclo) undergo isomerization as readily as the parent substances, the pseudoforms of the amides.



It appears also that oxygenimidoanhydrides,  , undergo a molecular rearrangement more readily than thioimidoanhydrides,  , and that among these labile forms the cyclo derivatives, in general, show the greatest stability. Before we undertook the investigation of this subject, it was known that certain cycloimidoesters undergo a molecular rearrangement on heating.

The first observation of this sort was made by Hofmann and Olshausen,[3] who showed that *o*-cyanuric methyl ester gave the

[1] *Ber. d. chem. Ges.*, **33**, 1467 (1900).
[2] *Am. Chem. J.*, **30**, July (1903).
[3] *Ber. d. chem. Ges.*, **3**, 272 (1870).

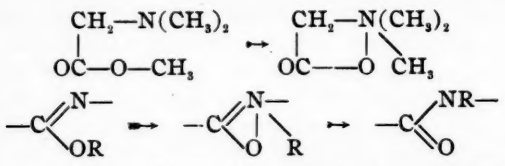
N-derivative on heating. Ponomaren[1] and Hofmann[2] then further investigated the subject. Haitinger and Lieben[3] found that methoxypyridine gave methylpyridon, and Knorr[4] found that methoxylepidine gave methyllepidon, facts which led Michael[5] to state that all compounds having the grouping ROCN would give the isomeres OCNR on heating.

In the pyrimidine series, such rearrangements were afterwards observed by E. v. Meyer[6] and by Pinner.[7] Andreocci[8] apparently found a similar case among the pyro- $\beta\beta'$-diazoles. Knorr and Fertig[9] further investigated the molecular rearrangement of alkyloxyquinoline derivatives by means of alkyl halides and showed that the reaction involved an addition. Wislicenus and Körber[10] showed that the 8-alkyloxycaffeins also undergo a metastatic change on heating. This appears to be a complete list of these molecular rearrangements in the cyclo series.

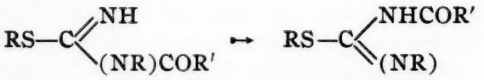
In the acyclo series Grabriel and Neumann[11] found that by the action of heat benzimidochlorethyl ester is transformed into β-chlorethylbenzamide, and the mechanism of this reaction was shown to involve an inner addition with the formation of an intermediate five-membered ring, by Wislicenus and Körber.[12] Recently the work on the molecular rearrangements of acycloimidoesters has been greatly extended by Lander.[13]

It is probable that the mechanism of these rearrangements by heat alone is similar to that in the case of the action of alkyl halides. A small quantity of foreign material may act catalytically, by addition and then a separation.[14] Or, under the influence of heat, this effect may take place within the molecule itself, as in the case of the molecular rearrangement of N-dialkylaminoesters into betaïnes.[15]

[1] *Ber. d. chem. Ges.*, **18**, 3271 (1855).
[2] *Ibid.*, **19**, 2061 (1896).
[3] *Monatsh. Chem.*, **6**, 323 (1885).
[4] *Am. Chem. J.*, **236**, 104 (1886).
[5] *J. prakt. Chem.*, **37**, 510 (1888).
[6] *Ibid.*, **39**, 271 (1889).
[7] Die Imidoaether u. Ihre Derivate, p. 215 (1892).
[8] *Ber. d. chem. Ges.*, **24**, R. 205 (1891).
[9] *Ibid.*, **30**, 922, 929; *Ibid.*, **30**, 937 (1897).
[10] *Ibid.*, **35**, 1991 (1902).
[11] *Ibid.*, **25**, 2383 (1892).
[12] *Ibid.*, **35**, 164 (1902).
[13] *J. Chem. Soc.* (London), **83**, 406 (1903).
[14] Compare Lander: *Loc. cit.*, p. 414.
[15] Willstätter: *Ber. d. chem. Ges.*, **35**, 585 (1902).



The three-membered, intermediate ring in the case of the imido-esters not being stable, the bonds shift and the stable amides are formed. In fact, this ring-formation is considered in a recent article,[1] by Kauffmann, to represent the structure of the pyridines. The molecular rearrangement of alkyloxypyridine derivatives therefore halts at what corresponds to the intermediate stage in other cases. Closely similar to these rearrangements are those of the imido acid anhydrides. Outwardly the molecular rearrangements of unsymmetrical acylthioureas, acylpseudothioureas[2] and their corresponding cyclo derivatives, the arylpseudothiohydantoïns, appear to be similar:



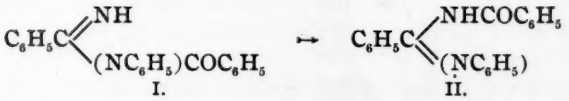
In these cases the mechanism, however, probably involves the formation of an unstable, four-membered ring as an intermediate condensation product.[3]

All of the unsymmetrical acylthiourea and acylpseudothiourea derivatives, which have been investigated, undergo the above represented isomerization on melting, and some so readily that they cannot be crystallized by warming with alcohol. Similar results would be expected in the true amidine series.

We first selected for examination benzenylphenyl amidine, $C_6H_5C(NH_2)=NC_6H_5$. Two molecular proportions of this substance were slowly treated in cold ether with benzoyl chloride. On filtering from the precipitate of amidine hydrochloride which formed, and evaporating the ether spontaneously in a vacuum, a crystalline benzoyl derivative was obtained. This material, when carefully prepared, was homogeneous, and it had the structure represented by formula I. When allowed to stand for some time, or,

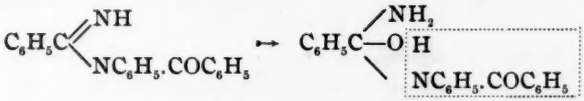
[1] *Ber. d. chem. Ges.*, **36**, 1062 (1903).
[2] *Am. Chem. J.*, **27**, 270 (1902).
[3] *Ibid.*, **28**, 134 (1902).

if an attempt was made to crystallize the substance from a hot solution, or if heated, it immediately underwent a molecular rearrangement into the isomeric benzoyl derivative, which is represented by formula II.

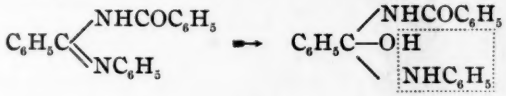


I. II.

The proof of this rearrangement was obtained as follows: When the material obtained directly from the ether solution was treated with dilute hydrochloric acid it underwent hydrolysis and gave practically the calculated quantity of benzanilide and benzamide. No dibenzamide was obtained.

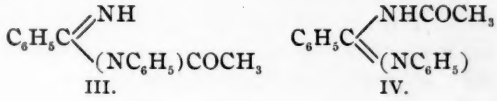


When another portion of the same preparation was warmed in a little alcohol for a few minutes on the steam-bath, and then treated with hydrochloric acid, the result obtained was precisely the reverse from the above; almost the calculated quantity of dibenzamide was obtained, while only a trace of benzanilide resulted. The hydrolysis took place in this case as follows:



The molecular rearrangement of unsymmetrical benzoylbenzenylphenylamidine therefore took place with great ease and smoothness.

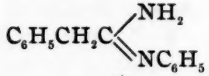
In our next experiment we employed the same benzenylphenylamidine, but used acetyl chloride instead of benzoyl chloride. In this case the product consisted of a mixture of the two following acetyl derivatives, corresponding to the above labile and stable benzoyl compounds.



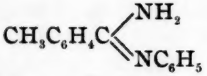
III. IV.

The structure of these products was determined by hydrolysis as before with hydrochloric acid. The remarkable fact was then discovered that the unsymmetrical acyl derivative III was a perfectly stable substance. It showed no tendency to rearrange even at a temperature of 150°-160°. This flagrant breach of analogy, as Lachman[1] states in other cases, certainly calls for protest from the systematists.

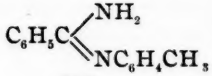
We next examined the behavior of the three following isomeric amidines with benzoyl chloride: Phenylacetphenylamidine (V), *p*-tolenylphenylamidine (VI), and benzenylorthotolylamidine (VII).



V.



VI.



VII.

Phenylacetphenylamidine (V) gave a mixture. This contained an unsymmetrical benzoyl derivative, which showed no tendency to undergo a molecular rearrangement. It could be repeatedly crystallized from alcohol and it could be heated above its melting-point without alteration.

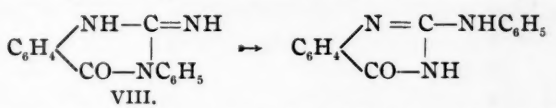
Paratolenylphenylamidine gave a mixture of the two isomeric benzoyl derivatives. That the unsymmetrical acyl derivative, contained in this mixture, readily undergoes a molecular rearrangement was shown by treating the product with dilute hydrochloric acid. Before heating, benzanilide was obtained; when the product was simply warmed on the steam-bath and then treated in the same manner with hydrochloric acid, no benzanilide resulted.

Benzenylorthotolylamidine gave the stable symmetrical amidine directly; the formation of an unsymmetrical derivative was not observed. These results show that the point of attack of acyl chlorides on the amidines differs in different cases and that both acyl derivatives may be formed together without involving a metastatic change. No conclusions as to whether a new unsymmetrical acyl amidine will or will not undergo a molecular rearrangement can be drawn from these experiments and no generalization can be made with the data at hand. The structure of the acyl amidines obtained gives no clue to the tautomeric form of the amidines beyond the probability that, in the cases where molecular rearrangements do take place,

[1] This Journal, **23**, 907 (1901).

the structure of the amidine corresponds to that of the stable form of the acyl derivative. The results also emphasize how unsafe it is to predict from analogy. They suggest that perhaps similar results may be observed in other series, the closely analogous imido acid anhydrides, for example.

In the course of the work, we found that, if pyridine was present, on treating an amidine with an acylchloride that diacyl derivatives resulted. We also examined the behavior of a cycloacylphenylguanidine on heating, *viz.*, 2-amino-3-phenyl-4-ketodihydroquinazoline (VIII). From its similarity in structure to benzoylbenzenylamidine and to the labile phenylpseudothiohydantoïn, which readily undergoes a metastatic change at 100°, a molecular rearrangement might be expected to take place in this case as follows:



VIII.

The material, however, proved to be quite stable and it sublimed unaltered at a high temperature.

EXPERIMENTAL PART.

Unsymmetrical Benzoylbenzylphenylamidine was prepared by slowly treating two molecular proportions of benzenylphenylamidine in ice-cold, dry ether with benzoyl chloride. The ether solution was then filtered and the filtrate evaporated in a vacuum. The crystalline mass thus produced, after washing with a little cold alcohol, melted at about 95°-97°, when carefully prepared. In a number of preparations it melted somewhat higher but then it was found to contain more or less of the isomeric symmetrical derivative. A nitrogen determination gave 9.8 per cent. nitrogen. Calculated for $C_{12}H_{10}ON_2$, 9.3 per cent. When an attempt was made to purify the material by crystallizing from alcohol, it underwent a molecular rearrangement into symmetrical benzoylbenzenylphenylamidine (melting-point 143°), which has already been described in a paper from this laboratory.[1]

Action of Hydrochloric Acid.—The material melting at 95°-97° (0.95 gram) was treated with 2 cc. of alcohol and 2 cc. of 22 per cent. hydrochloric acid. The amidine dissolved and then a mass of crystals separated; the whole was warmed to boiling, cooled

[1] *Am. Chem. J.*, **20**, 573 (1898).

and then treated with 9 cc. of 15 per cent. sodium hydroxide solution. The insoluble material was washed with 12 cc. of water; it melted at 156°-159° and it weighed 0.60 gram. This proved to be benzanilide, the calculated quantity of benzanilide being 0.62 gram. On acidifying the alkaline solution with acetic acid no precipitate was formed. This shows the absence of dibenzamide and of the symmetrical benzoyl derivative in the original material. On shaking the solution with ether, benzamide was extracted.

Behavior on Heating.—Another portion of the benzoyl derivative melting at 95°-97° (0.95 gram) was warmed on the water-bath in 10 cc. of alcohol for a half hour. The alcohol was then evaporated and the varnish obtained was treated with 2 cc. of hydrochloric acid as above, except that no alcohol was used. On gently warming, the varnish solidified to a mass of colorless needles. When washed with water and dried, this weighed 0.62 gram. This all dissolved in 5 cc. of 15 per cent. alkali diluted with 5 cc. of water, except 0.03 gram of material, and was precipitated by acetic acid. It melted at 145°-147° and had all the properties of dibenzamide, the yield being about 87 per cent. of the calculated. These results prove conclusively that a rearrangement of the unsymmetrical benzoyl derivative took place on heating.

Unsymmetrical Acetylbenzenylphenylamidine.—The product, in this case, on evaporating the ether, formed a varnish which finally solidified. It then melted at about 114° and when mixed with acetanilide the melting-point was lowered to 90°-95°. It crystallized from alcohol in the form of colorless prisms and then melted at 128°-129°; when this was mixed with benzamide the melting-point was lowered to 110°. A nitrogen determination gave 11.41 per cent. nitrogen. Calculated for $C_{15}H_{14}ON_2$, 11.76 per cent. The alcoholic mother-liquors from the above were allowed to stand at ordinary temperature, whereupon prisms of the symmetrical acetylbenzylphenylamidine melting at 138°-139° were obtained. This was described in a previous article.[1]

Action of Hydrochloric Acid.—The above acetyl derivative melting at 128°-129° was warmed in alcohol with hydrochloric acid, the alcohol was evaporated, and the residue on crystallizing from water gave plates of acetanilide melting at 112°-113°.

[1] *Am. Chem. J.*, **20**, 574 (1898).

Behavior on Heating.—The acetyl derivative, which was proved to have an unsymmetrical structure by the above experiment, was heated at various temperatures and finally for two hours at 150°-160°. A slight decomposition took place, but on crystallizing from benzene unaltered material was obtained. When mixed with the symmetrical derivative the melting-point was lowered to 108°-115°. There was no evidence of a rearrangement having taken place. Owing to the difficulty with which the following amidines dissolve in ether, chloroform was tried as a solvent in some of the experiments. The results were not satisfactory, as decomposition products were formed which interfered with the isolation of the acyl amidines. The best results were obtained when the amidines were simply suspended in dry ether and allowed to stand for some time with the required amount of benzoyl chloride.

Benzoylphenylacetamide, $C_6H_5CONHCOCH_2C_6H_5$.—This was formed along with benzanilide and other products when phenylacetphenylamidine was treated with benzoyl chloride in chloroform. The hydrochloric acid salt of the amidine did not separate in this case but was removed in the subsequent treatment with water. The product was a semi-solid mass which, when dissolved in benzene, gave benzanilide and then colorless prisms which, after several recrystallizations, melted at 129°-130°. A nitrogen determination agreed with the calculated for benzoylphenylacetamide. Calculated for $C_{15}H_{13}O_2N$, 5.8 per cent. Found, 6.1 per cent. The material was soluble in cold alkali.

Unsymmetrical Benzoylphenylacetphenylamidine.—Ten grams of phenylacetphenylamidine were suspended in 100 cc. of dry ether, and after 3.3 grams of benzoyl chloride had been added the mixture was allowed to stand four hours. The solid material then removed by filtration was found to dissolve completely in water and was therefore the hydrochloric acid salt of the amidine. After the ether solution was evaporated, a gum remained which did not crystallize on standing. When dissolved in alcohol, it gave colorless plates which, after three recrystallizations from alcohol, melted at 110°-111°. The liquid was slightly cloudy up to 118°. A nitrogen determination gave results agreeing with the calculated for a monobenzoylphenylacetphenylamidine. Calculated for $C_{21}H_{18}ON_2$, 8.9 per cent. Found, 8.6 per cent.

Action of Hydrochloric Acid.—One-half a gram of the material melting at 110°-111° was treated with hydrochloric acid, as in the previous cases, whereupon the leaf-like crystals of benzanilide were obtained, melting at 157°-158°. When this benzoyl derivative was heated above its melting-point (140°) and then crystallized from alcohol, the melting-point rose to 122°-123°, but, on treating this material with hydrochloric acid, little or no benzoylphenylacetamide was obtained.

Dibenzoylphenylacetphenylamidine was prepared by mixing in chloroform, 4.4 grams of the amidine, 1.6 grams of pyridine and 2.9 grams of benzoyl chloride, the latter diluted with ether. The precipitate which formed consisted of the hydrochloride of the amidine. The chloroform contained material which, on crystallizing from alcohol, formed colorless prisms and melted at 175°. A nitrogen determination gave 7.2 per cent. nitrogen. Calculated 6.7 per cent. When treated with hydrochloric acid, benzanilide, phenylacetamide and benzoic acid were obtained.

Symmetrical Benzoylparatolenylphenylamidine.—Paratolenylphenylamidine (6.1 grams) suspended in 100 cc. of dry ether was treated with 2 grams of benzoyl chloride in 25 cc. of ether. The mixture was allowed to stand for three hours. On filtering and evaporating the ether, a gummy mass was obtained which, on crystallizing from alcohol, gave clusters of colorless prisms melting at 126°. A nitrogen determination showed that this substance was a monobenzoylparatolenylphenylamidine. Calculated for $C_{21}H_{18}ON_2$, 8.91 per cent. Found, 8.82 per cent.

Action of Hydrochloric Acid.—One gram of the material was suspended in alcohol and warmed with a few drops of hydrochloric acid. On standing, colorless needles separated which, on crystallizing from alcohol melted sharply at 112°-113°. A nitrogen determination indicated that this substance was *paratoluylbenzamide*, $CH_3C_6H_4CONHCOC_6H_5$. Calculated for $C_{15}H_{13}O_2N$, 5.85 per cent. Found, 6.34 per cent. That this was the diacyl amide was further shown by the fact that the material dissolved in alkali and was decomposed into paratoluic amide melting at 151°-157°. The unsymmetrical benzoyl derivative in this case was not isolated in a state of purity. That it was present in the gummy mass described above was shown by the fact that benzanilide was obtained when the product was treated with dilute hydrochloric

acid. A portion of the crude reaction product was warmed on the steam-bath and then treated with hydrochloric acid, whereupon no benzanilide was obtained.

Dibenzoylbenzenylorthotolylamidine.—Ten grams of benzenylorthotolylamidine were suspended in 100 cc. of dry ether and treated with 3.3 grams of benzoyl chloride in 20 cc. of ether. The mixture was then allowed to stand over night. The amidine hydrochloride which separated was mixed with some material which did not dissolve when the mixture was treated with water. When this material was crystallized from alcohol, colorless, beautiful, diamond-shaped plates were obtained, melting sharply at 167°. A nitrogen determination showed that this material was a dibenzoyl derivative: Calculated for $C_{28}H_{22}O_2N_2$, 6.7 per cent. Found, 7.0 per cent. When this substance was treated with dilute hydrochloric acid in alcohol, crystals of benzorthotoluide separated melting at 142°.

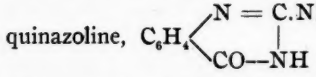
Symmetrical Benzoylbenzenylorthotolylamidine.—On evaporating the ether solution from the above dibenzoyl derivative, a varnish was obtained. From this, on crystallizing from alcohol, colorless prisms were obtained melting at 111°-113°. A nitrogen determination gave 8.9 per cent. Calculated for $C_{21}H_{18}ON_2$, 8.9 per cent.

Action of Hydrochloric Acid.—A gram of the substance was treated with dilute hydrochloric acid (2 cc.) and 2 cc. of alcohol. From this solution long, colorless needles of dibenzamide separated, melting at 148°. When these needles were mixed with dibenzamide the melting-point was not lowered.

Orthophenylguanidinebenzoic Acid,

$C_6H_4\begin{cases}NH.C(NH)—NHC_6H_5\\COOH\end{cases}$

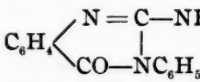
.—In the course of some experiments with pseudothioureas we heated orthoaminobenzoic acid with phenylpseudomethylthiourea and obtained a product which crystallized from alcohol in colorless prisms, melting at 248°. This material was not dissolved at first by sodium hydroxide or hydrochloric acid, but on standing in these solvents it underwent a change, being converted into a substance, crystallizing in hair-like needles from alcohol, melting at 256°. This latter material was readily soluble in alkali, and a nitrogen determination gave

results agreeing with the calculated for 2-anilino-4-ketodihydroquinazoline,  . Found, 17.67 per cent. Calculated for $C_{14}H_{11}ON_3$, 17.72 per cent.

At this point we were unable to decide whether the above product first obtained, melting at 248°, underwent a direct condensation into the above quinazoline derivative soluble in alkali, or whether it first condensed to give the isomeric 2-amino-3-phenyl-4-ketodihydroquinazoline, which would be insoluble in alkali, this then undergoing a molecular rearrangement into the above quinazoline, melting at 256°. To decide this question we prepared 2-amino-3-phenyl-4-ketodihydroquinazoline from *2-Chlor-3 phenyl-4-ketodihydroquinazoline.*—This chloride was prepared from 2-thio-3-phenyl-4-ketotetrahydroquinazoline by following the directions of McCoy.[1]

McCoy obtained this chloride, but did not purify the substance. We found that the oil first obtained solidified and could be crystallized from alcohol. It then formed colorless prisms and melted at 132°. It was analyzed with the following results: Calculated for $C_{14}H_9ON_2Cl$, 10.9 per cent. nitrogen. Found, 10.7 and 11.1 per cent.

2-Amino-3-phenyl-4-ketodihydroquinazoline,



The above chloride was heated in a closed tube at 120°-130° with an excess of alcoholic ammonia. The product crystallized from alcohol in colorless prisms and melted at 237°-238°. It was insoluble in sodium hydroxide, as was expected, and a nitrogen determination gave: 17.50 per cent. nitrogen. Calculated for $C_{14}H_{11}ON_3$, 17.72 per cent. When this material was boiled with dilute hydrochloric acid, complete solution finally took place and, on cooling, 3-phenyl-2,4-diketotetrahydroquinazoline[2] separated. When the above cyclcacylguanidine was heated above its melting-point (in a bath at 250°), it simply sublimed unaltered without undergoing any molecular rearrangement.

[1] *Ber. d. chem. Ges.*, **30**, 1691 (1897).

[2] Busch: *J. prakt. Chem.*, **51**, 265 (1895); Paul: *Ber. d. chem. Ges.*, **27**, 978 (1894).

NEW HAVEN, CONN., May 26, 1903.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

MERCUROUS SULPHIDE.

BY CHAS. BASKERVILLE.

Received May 25, 1903.

IN the paper "On the Reactions between Mercury and Concentrated Sulphuric Acid,"[1] by F. W. Miller and the writer, two statements were made, which, while true for the conditions given, require modification in the light of knowledge recently gained. "The reaction is by no means like that of copper"[2] (p. 874) and "No sulphide was produced, nor any free sulphur" (p. 876). By great variations of one of the factors, time, sulphide was obtained. The experiment was continued through a period of five years and one week. Ten grams of pure mercury[3] were covered with 50 grams of chemically pure sulphuric acid (99.65 per cent.) in a well-ground, glass-stoppered bottle of about 100 cc. capacity and allowed to remain at the temperature of the laboratory (never over 30° C.) for the period mentioned. While the bottle was never subjected to the direct rays of the sun, no attempt was made to shield it from the light.

When the bottle was opened, there was a strong outward pressure, and noticeable quantities of sulphur dioxide escaped. This corroborates the statements put forward in our second paper[4] in controversion of the criticism of Pitman.[5] Morley[6] and Berthelot[7] have also shown, independently, that mercury and sulphuric acid of maximum concentration react at ordinary temperatures with the evolution of sulphur dioxide.

The point of especial interest in the experiment lay in the simultaneous formation of a sulphide of mercury, which showed that the mercury resembles copper in this reaction more than was thought. Upon the bright metal there separated flakes, which resembled plates, of mercurous sulphide. The acid was decanted, a large volume of water added and quickly decanted. This was

[1] This Journal, **19**, Nov., 1897.
[2] *Ibid.*, **17**, Nov., 1895, and **18**, Nov., 1896.
[3] *Loc. cit.*
[4] This Journal, **20**, 515.
[5] *Ibid.*, **20**, 100.
[6] *Loc. cit.*
[7] *Chem. News*, **76**, 325; *Compt. rend.*, **125**, 20.

done several times. The bottle was inclined and revolved so that most of the sulphide was caused to cling to the sides of the vessel, the metallic mercury poured out and the sulphide thrown upon a filter and washed with alcohol (95 per cent.) until the wash-water was no longer acid. The brownish black plates (about 0.2 gram) were dried at 110° C. and analyzed by Mr. R. O. E. Davis of this laboratory.

Amount taken.	Sulphur found. Per cent.	Mercury found. Per cent.	Calculated for Hg_2S.
0.0866	8.23	....	7.41
0.0707	...	91.94	92.59
Total	...	100.17	100.00

The quantity remaining was too small to examine for the presence of free sulphur, although from the analysis it appears that 0.82 per cent. of free sulphur was present. As no quantitative determination of the sulphur dioxide, mercury sulphates produced, and so forth, were made, it is impossible to indicate the course of the reaction by an equation.

Authoritative works (Richter, Dammer, etc.) state that mercurous sulphide is not definitely known. Berzelius[1] said the black precipitate produced by hydrogen sulphide with mercurous salts was mercurous sulphide, but Barfoed[2] has shown that it is a mixture of mercuric sulphide and mercury. Antony and Sestini[3] state that hydrogen monosulphide acting upon mercurous salts below 0° C. give mercurous sulphide, which above that temperature decomposes into mercuric sulphide and mercury.

Mercurous sulphide heated in a closed tube turns white (doubtless due to oxidation), becomes slightly yellow, then melts to a dark orange-brown liquid, which changes to a white solid on cooling, as does mercurous sulphate.

[1] *Archiv. d. Apothekervereins im nördl. Deutschland, von Brandes*, **18**, 292.
[2] *J. prakt. Chem.*, **93**, 230.
[3] *Gazz. chim. Ital.*, **24**, I, 193.

UNIVERSITY OF NORTH CAROLINA,
May 8, 1903.

THE ACTION OF METALLIC MAGNESIUM UPON AQUEOUS SOLUTIONS.

By Charlotte F. Roberts and Louise Brown.

Received May 27, 1903.

The paper read by Mr. Kahlenberg on the above subject, at the Washington meeting of the American Chemical Society, interested us so much that we undertook a few simple experiments in the same line for ourselves. Since his paper has appeared in print[1] we find that in a few particulars our results differ from his and that our experiments have been carried on along somewhat different lines, and it has therefore seemed possible that our results also might be of interest to others.

In all of our experiments the *modus operandi* was the same. A 100 cc. gas-measuring tube was filled with the solution to be employed. In the mouth of this tube a one-holed rubber stopper was inserted, and a piece of magnesium ribbon was held in place in the solution by fastening it to the stopper with a bit of cheese-cloth and some thread. The whole was then set up, in most cases in a tall jacket containing more of the same solution, for convenience in measuring, frequently, the volume of the gas under atmospheric pressure. The magnesium used was the magnesium ribbon manufactured by Schuchardt, and in our experiments the *solution* was always in excess. We used in most of our experiments an amount of magnesium equivalent to about 50 cc. of gas, or a piece about 8 cm. in length.

The most important particular in which our results differed from those of Mr. Kahlenberg was in the action of magnesium on distilled water. We found that if we used ammonia-free water, freshly boiled to drive out dissolved gases, no gas collected in the tube. The experiment was tried first with a short strip of magnesium ribbon and left standing for a week. It was then repeated with a strip of magnesium ribbon 50 cm. in length and left standing for four weeks. The magnesium appeared slightly tarnished, but no trace of gas was visible at the end of that time. When *unboiled* distilled water was used, in the same length of time, with much smaller amounts of magnesium, varying amounts

[1] This Journal, **25**, 380.

of gas, from 2 to 3 cc., were collected. These results are apparently in opposition to those obtained by Bryant, who states that boiled and unboiled water have the same effect on magnesium.[1]

The experiment was tried of taking some of the pure boiled distilled water and passing a current of oxygen through it before setting up the apparatus. In this case gas began to collect after standing twenty-four hours, and in the course of two weeks, 2.7 cc. of gas had collected from a strip of magnesium about 8 cm. in length. When a similar experiment was tried, using carbon dioxide instead of oxygen, the escape of gas was, as might have been expected, very rapid, the rate being greatest at first and decreasing with the time, as with other acids.

The principal facts indicated by our experiments seem to be:

(1) That magnesium is without action on distilled water, boiled to free it from gases and carefully cooled out of contact with air.

(2) That magnesium acts on undistilled water and on unboiled distilled water, setting free varying amounts of gas; also on water boiled and afterward charged with oxygen or carbon dioxide.

(3) That the hydrogen equivalent of magnesium can be obtained from aqueous solutions of varying strengths of the chlorides of sodium, potassium, magnesium, barium, calcium and strontium; also very slowly from the sulphate of magnesium (probably also of sodium and potassium); also from such dilute solutions of hydrochloric and sulphuric acids as contain in themselves but a small proportion of the hydrogen liberated.

(4) That with the same surface of magnesium the action of the chlorides is much more rapid than that of the corresponding sulphates. With chlorides of the same metal, the rate is dependent upon the concentration, though no strict proportionality can be traced. The maximum rate is more quickly attained in the stronger solution than in the weaker and is greater in amount, but the length of time for completing the reaction does not differ very much in the two cases.

(5) With equimolecular solutions of chlorides of sodium, potassium, magnesium, calcium, strontium and barium, the order of rapidity of action upon magnesium ribbon in our experiments was as follows: Magnesium, barium, strontium, calcium, sodium and potassium.

[1] *Chem. News*, Nov. 3, 1899.

In such experiments as these it is, of course, impossible to determine exactly the end-point of the reaction or to measure with any accuracy the rate of the reaction as it approaches completion. Occasional tapping of the tube is necessary to liberate the last portions of gas, and there is always the possibility that some magnesium may be covered by the precipitate and left unacted upon. We observed, however, what was mentioned by Mr. Kahlenberg, *viz.*, that the coating of precipitate over the magnesium did not retard the action as much as might have been expected. Even when the magnesium ribbon appeared to be entirely crusted over, the reaction went on until approximately the hydrogen equivalent of the magnesium had been collected. It is true that the results as shown in the following tables run a little low, but considering the possible sources of error, they seem near enough to justify the statement that the hydrogen equivalent may be set free in all cases.

TABLE I.

(Solutions contained $^1/_{10}$ gram-mol. per liter.)

	Weight of magnesium calculated from gas.	Weight of magnesium taken.
$MgCl_2$	0.0538	0.0539
KCl	0.0535	0.0539
NaCl	0.0525	0.0539
$BaCl_2$	0.05345	0.0540
$CaCl_2$	0.05276	0.0534
$SrCl_2$	0.0526	0.0534
$MgSO_4$	0.0530	0.0539

Although but one result is given, confirmatory experiments were made in almost every case.

The time required for the completion of the reaction, with the amounts above given, was from twenty-four to forty-eight hours in the case of the chlorides, but in the case of the sulphates was much greater. The sulphates of sodium, potassium and magnesium were all tried, and the one which acted most rapidly was magnesium. With this it took nearly four weeks to get the result above given. With the sulphates of sodium and potassium the action was so slow that the experiment was discontinued before the reaction was completed.

That very dilute solutions of the chloride of magnesium are adequate to set free the hydrogen equivalent of the magnesium is indicated by our experiments with very dilute hydrochloric

acid. The acid used was of such strength that from 100 cc. only 8.1 cc. of hydrogen could be set free. The tube was inverted in a small dish containing more of the same liquid, and this might increase the possible yield of hydrogen by a small amount. The apparatus was left standing for a week, although the operation was probably completed a little before that time. At the end of a week, the volume of hydrogen was 52.5 cc. at a temperature of 19° C. and pressure of 765 mm. This corresponds to 0.0540 gram of magnesium, and the weight of magnesium taken was 0.0539 gram. A study of the rate of this reaction per twenty-four hours is interesting.

TABLE II.

	Volume of gas collected.	Volume increment per hour.
1st 24 hours	5.2	0.22
2nd 24 hours	7.8	0.1
3rd 24 hours	17.6	0.4
4th 24 hours	29.8	0.5
8 hours later	35.1	0.66
6th 24 hours	48.0	0.32
7th 24 hours	52.5	0.19

The relation between the time and the amount of gas collected is therefore represented by the following curve:

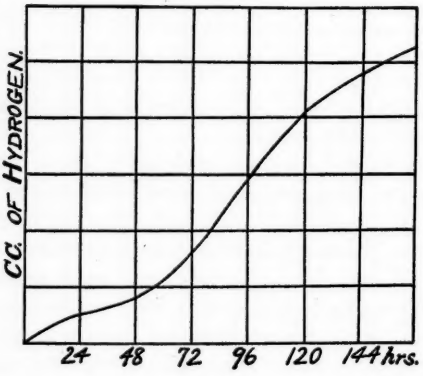


Fig. 1.

It will be noticed that the *rate* of the reaction at first decreases with the time, as is usual with the action of an acid on a metal; then, when an amount of gas has been collected nearly equal

to the amount calculated as contained in the hydrochloric acid used, the rate increases until it reaches a maximum and then decreases in about the same way as has been observed when the metal was put directly into a solution of magnesium chloride. In this case, when the rate began to increase, the amount of magnesium which had gone into solution as magnesium chloride can not have been greater than 10 milligrams.

As has just been indicated, we observed that the curve showing the relation between the *time* and the *volume increment* in a given time was distinctly different in the case of the action of acid in excess upon magnesium, and the action of aqueous solutions of chlorides. This is shown in the following table:

TABLE III.

	HCl. (Weight magnesium taken = 0.0536.)		$MgCl_2$. 1/6 molecule per liter. (Weight magnesium taken = 0.0539.)	
	Volume of gas.	Rate per hour.	Volume of gas.	Rate per hour.
1 hour	11.6	11.6	0.9	0.9
2 hours	18.2	6.6	3.9	3.0
3 "	21.8	3.6	8.7	4.8
4 "	24.1	2.3	13.3	4.6
5 "	26.1	2.0	17.6	4.3
6 "	27.7	1.6	21.3	3.7
7 "	...	..	24.8	3.5
8 "	...	..	28.3	3.5
9 "	...	..	31.6	3.3
10 "	...	..	34.2	2.6
11 "	...	..	36.4	2.2

These data and corresponding ones in regard to certain other solutions are represented in the following curves, which show how the volume increment per hour changes as time advances. It will be observed that the acid-rate curve is a rapidly descending one, according to the law of mass action, whereas in the case of the chlorides, the curve ascends in each case until it reaches a maximum and then descends slowly.

The maximum rate depends upon the particular chloride employed and upon the strength of the solution. With different concentrations of the same salt, the maximum rate is higher in the case of a strong solution than with a weak one and is, in general, more quickly attained. The curves also show that after the maximum rate has been reached, there is a tendency for the rates to approach one another, so that after four or five hours, the volume

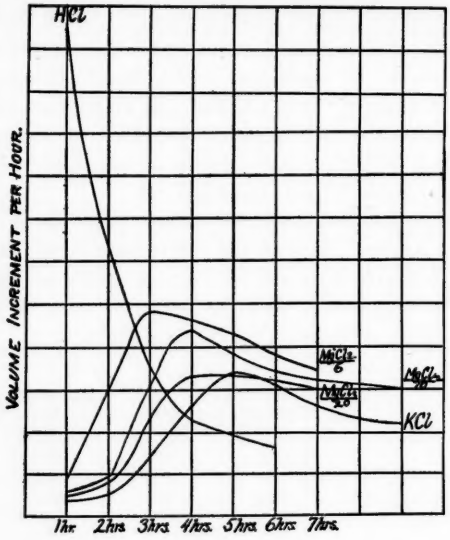


Fig. 2.

increments per hour do not vary much with the different concentrations.

Although Mouraour and others have stated that the action of magnesium on solutions of the alkaline earth metals is feeble, it was not our experience that the rate of the reaction with these substances fell so very far behind that on solutions of the same strength of magnesium chloride. In order to compare the rates of action of the chlorides of the alkali and alkaline earth metals, solutions containing $^1/_{10}$ gram-mol. per liter were set up as nearly as possible at the same time; pieces of magnesium ribbon 33 cm. long were used and observations taken every half hour. A solution of magnesium chloride containing $^3/_{10}$ gram-mol. per liter was also used. The results of these experiments are expressed in the following table:

TABLE IV.

Volume of gas collected.

	KCl.	NaCl.	$CaCl_2$.	$SrCl_2$.	$BaCl_2$.	$MgCl_2$.	$^3/_{10}MgCl_2$.
1 hour.....	0.7	1.7	2.2	2.3	3.0	3.3	3.2
2 hours.....	3.5	5.6	6.6	7.0	9.9	11.6	13.8
3 "	9.0	11.8	13.2	14.3	21.2	24.6	29.8
4 "	16.6	19.5	22.7	24.1	34.4	37.5	42.4

	KCl.	NaCl.	$CaCl_2$.	$SrCl_2$.	$BaCl_2$.	$MgCl_2$.	$^3/_{10}$ $MgCl_2$.
5 hours.....	25.0	27.4	32.1	33.8	45.5	48.7	54.0
6 "	33.8	35.3	41.0	43.0	55.3	59.3	64.8
7 "	41.6	42.6	48.8	51.6	64.3	69.6	74.6
8 "	...	49.4	56.0	59.8	72.5	78.4	83.4

Volume increment per hour.

	KCl.	NaCl.	$CaCl_2$.	$SrCl_2$.	$BaCl_2$.	$MgCl_2$.	$^3/_{10}MgCl_2$.
1 hour.....	0.7	1.7	2.2	2.3	3.0	3.3	3.2
2 hours.....	2.8	3.9	4.4	4.7	6.9	8.3	10.6
3 "	5.5	6.2	6.6	7.3	11.3	13.0	16.0
4 "	7.6	7.7	9.5	9.8	13.2	12.9	12.6
5 "	8.4	7.9	9.4	9.7	11.1	11.2	11.6
6 "	8.8	7.8	8.9	9.2	9.8	10.6	10.8
7 "	7.8	7.3	7.8	8.6	9.0	10.3	9.8
8 "	..	6.8	7.2	8.2	8.2	8.8	8.8

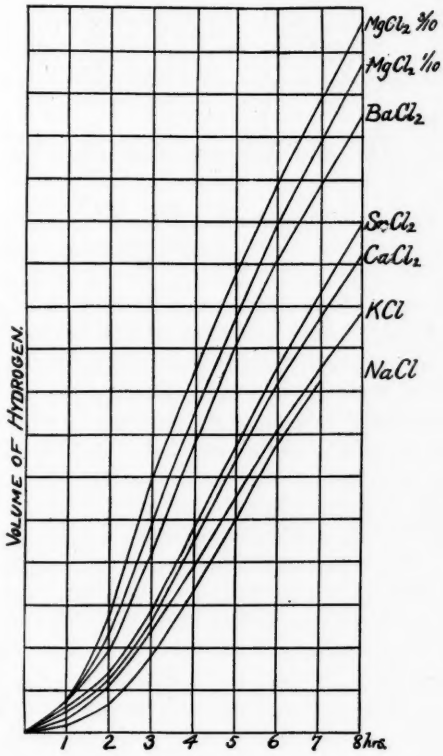


Fig. 3.

The curves representing the relation between the time and the volume of gas collected show at a glance the similarity in action of the sodium and potassium chlorides, and also of the chlorides

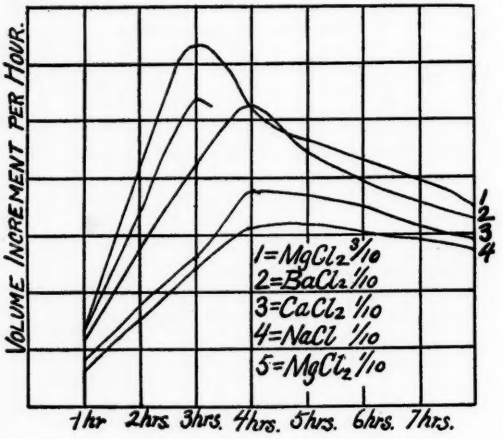


Fig. 4.

of calcium and strontium, but that the action of the barium salt is more nearly like that of the magnesium chloride than like that of the other alkaline earth chlorides. It will be noticed that the chloride of magnesium attains its maximum rate in the third hour, the salts of the alkaline earth metals in the fourth hour, and of sodium and potassium in the fifth and sixth hours; also that the sodium begins more rapidly than the potassium, but that the potassium gradually gains upon the sodium. In all cases, the *rate* of the reaction at first increases and then decreases, as is shown in the accompanying graphic representation of the relation between the time and the volume increments per hour. The potassium and strontium curves are omitted because they correspond so nearly with the sodium and calcium, and the curve of the weaker magnesium chloride solution is only given in part, because, after passing the maximum, it coincides in various parts with the barium chloride and the stronger magnesium chloride. It is noteworthy that the curves, which reach the highest maxima, descend the most rapidly, and therefore there is a tendency to approach a uniform rate. It should perhaps be mentioned that the hydrogen equivalent of the magnesium used would be about 200 cc., so that these observations were made only during the first part of the reaction.

The persistency of type of the rate curve in all these salts, consisting as it does of an ascending and then a descending portion, seems to us of sufficient importance to be taken into account in any explanation of the phenomenon.

CHEMICAL LABORATORY OF WELLESLEY COLLEGE,
WELLESLEY, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI, NO. 59.]

A METHOD FOR THE DETECTION OF CHLORIDES, BROMIDES AND IODIDES.[1]

BY STANLEY BENEDICT AND J. F. SNELL.

Received June 5, 1903.

THE problem of the detection of chlorides, bromides and iodides in presence of each other is one to which a great deal of attention has been devoted, and the present proposal of a new method is justified only by the conviction of the authors that in simplicity of execution, in reliability and in delicacy this method is superior to any hitherto proposed.

Like many of the methods proposed in the past, the one here presented is based upon the varying ease of oxidation of the halogen acids. It arose from a reasonably successful attempt to use dilute nitric acid as the oxidizing agent. Concentrated nitric acid, added dropwise, was employed for this purpose by Kebler,[2] who states that during a five years' trial by students it gave very satisfactory results. We have found that if nitric acid of suitable dilution is used, it is indeed possible to boil a mixture of the halogen salts with it long enough to liberate and expel all the iodine and bromine without any noticeable loss of chlorine. We may cite here two out of about twenty-five experiments. The acid was of five times molar strength and the quantity used was about half the volume of the solution to be tested:

1. Cl detected in a mixture of 49.9 cc. N KBr and 0.1 cc. N NaCl.
2. Cl detected in a mixture of 10 cc. N/100 KI, 9.8 cc. N/100 KBr, and 0.3 cc. N/100 NaCl.

The substitution of dilute for concentrated nitric acid obviates one defect in Kebler's method, *viz.*, that the concentration of the

[1] Read before the Cincinnati Section of the American Chemical Society, May 13, 1903.
[2] *J. Anal. Appl. Chem.*, **6**, 569 (1892).

acid in the test solution was not well enough controlled, but there are at least two objections that apply to the method, even when the dilute reagent is used, *viz.*, that the separation between iodide and bromide is by no means sharp and that in some instances iodic acid is formed in sufficient quantity to give a precipitate with silver nitrate resembling silver chloride. In the course of the experiments referred to above we observed in several instances that a solution of pure potassium iodide, after boiling with dilute nitric acid until colorless, would give with silver nitrate a white precipitate, soluble in ammonium hydroxide (therefore not iodide) and that this precipitate was not obtained from another portion of the decolorized solution after neutralizing with ammonia, acidifying with oxalic acid, evaporating to dryness and redissolving in nitric acid (therefore iodate). Another fact noticed in the course of these experiments was that a solution containing both potassium bromide and potassium iodide was decolorized somewhat more quickly than a solution of bromide alone. This also pointed to the conclusion that some iodic acid was formed by the action of the nitric acid on the liberated iodine, for the hydrobromic acid would be oxidized more readily by iodic than by nitric acid.

It was the above-mentioned observation that led to the use of the reagent proposed in our present method, *viz.*, iodic acid in the form of potassium iodate. This oxidizing agent will not react with any of the halide ions in neutral solution, but will liberate iodine from potassium iodide in acetic acid solution, while the bromine of potassium bromide is not at all liberated, except upon addition of a stronger acid. As the stronger acid for liberating the bromine we employ nitric acid (dilute) for the two reasons that in the presence of this acid it is easy to eliminate any excess of potassium iodate and that, on the other hand, should the quantity of potassium iodate added be insufficient to react with all the bromide, the nitric acid is itself capable of effecting a complete separation. The first reason is the main one, as, in general, the quantity of potassium iodate added will be sufficient to react with all the bromide.

According to Fresenius,[1] the use of iodic acid or of potassium iodate and hydrochloric acid as a reagent for iodides was proposed by Liebig. Fresenius objects that the reagent "must be

[1] "Qualitative Analysis," Wells' translation (1897), p. 380.

used with the greatest caution" because "an excess of iodic acid will at once put an end to the reaction." It is obvious that this objection applies only to the use of the iodate *with hydrochloric acid,* the liberated iodine combining with the chlorine to form iodine chloride. In the absence of hydrochloric acid no such difficulty exists. Another objection made by Fresenius is that reducing agents will liberate iodine from the reagent, thus causing confusion. In reply to this objection we would point out that the halogen acids can be easily separated from all the other common acids, with the exception of sulphocyanic, by precipitating in presence of nitric acid with silver nitrate and reducing the precipitate with zinc and sulphuric acid.[1] The silver sulphocyanate could easily be destroyed by igniting the precipitate before reducing it, but this is unnecessary. In the presence of sulphocyanate, the test for iodide may be made (after neutralizing) by adding first sodium acetate and then acetic acid and potassium iodate. It is a familiar fact that the acidity of acetic acid is diminished by the addition of sodium acetate, the increase in the concentration of the acetate ion causing a depression of the dissociation of the acid. In such a solution, *i.e.,* in one containing an extremely low concentration of hydrogen ions, the reaction between the sulphocyanate and iodate is entirely prevented, while that between the iodide and iodate still takes place.

Both of the reagents that Fresenius mentions, *viz.,* free iodic acid and potassium iodate with hydrochloric acid, have, of course, the further disadvantage that they cannot be used in presence of bromides, since they liberate bromine as well as iodine. But potassium iodate with acetic acid is free from this objection, as well as from those raised by Fresenius and has the obvious advantages over the commonly employed reagent, chlorine water, that the quantity of iodine liberated is one-fifth greater and that there is absolutely no danger of decolorization of the liberated iodine by excess of the reagent. For the detection of bromides, potassium iodate with nitric acid has similar advantages over chlorine water, the danger of decolorization by excess being absent and six halogen atoms being liberated instead of five, but here we have the additional advantage that the sixth halogen atom is iodine instead of bromine and that consequently the color imparted to the solution, whether in water, carbon disulphide or chloroform, is more intense.

[1] See Bailey and Cady's "Qualitative Analysis," (1901), p. 209.

The superior delicacy of the iodate reagent indicated by the above considerations is amply borne out by the results of actual tests. Thus, using 5 cc. of solution and shaking with about 1 cc. of freshly decolorized carbon disulphide, we were able to detect iodine by use of potassium iodate and acetic acid in an N/60,000 solution of potassium iodide without failure and in one trial out of two in an N/90,000 solution, while chlorine water gave a very faint test upon the third trial with an N/40,000 and failed entirely with an N/50,000 solution. Testing in the same manner for bromides, using potassium iodate and dilute nitric acid, we obtained coloration of the disulphide from an N/16,000 solution of potassium bromide on warming slightly, while chlorine water gave the test in an N/2,500 solution (which is about the delicacy claimed by Fresenius, *viz.*, 1 part of bromine to 30,000 of solution),[1] while it failed entirely with an N/4,000 solution. It would appear from these results that the iodate is nearly twice as delicate a reagent as chlorine water for iodides and four or five times as delicate a reagent for bromides, and with freshly decolorized carbon disulphide is capable of detecting iodine in 5 cc. of a solution containing 1 part of iodine in 500,000 of solution and bromine in 5 cc. of a solution containing 1 part of bromine in 200,000 of solution. It may be remarked in this connection that while the color test for iodine or bromine is decidedly more delicate with carbon disulphide than with chloroform, the latter reagent is sufficiently delicate for ordinary purposes and is, perhaps, preferable as a laboratory reagent because it does not become colored on standing.

METHOD.

The separation of the three halogens can be conveniently accomplished in a rather wide (say 2 cm.) test-tube in which a liquid can be boiled without loss from bumping. The whole analysis does not take more than ten minutes. The reagents used are neutral potassium iodate of one-tenth, potassium iodide of one-fifth, and nitric acid of five times molar concentration. (Specific gravity of the nitric acid = 1.18.) The procedure is the following:

(*a*) To the neutral solution add potassium iodate and acidify with acetic acid. Coloration shows the presence of iodide, which may be confirmed by shaking a portion with chloroform or carbon disulphide.

[1] *Loc. cit.*, p. 359.

(*b*) If iodide is found, add a little more potassium iodate to the main portion of the solution and boil. Repeat this procedure until further addition of iodate fails to produce coloration, but avoid more than a slight excess of iodate. Having expelled the liberated iodine by boiling, add to the solution nearly one-half its volume of dilute nitric acid. Coloration shows bromide, which may be confirmed by shaking a portion with chloroform or carbon disulphide.

(*c*) Boil the main portion of the solution until colorless, add 1 or 2 cc. of potassium iodide and boil again until colorless. The potassium iodide reduces the excess of iodate and the excess of iodide added is destroyed by the nitric acid. Boil again until perfectly colorless, then add an equal volume of concentrated nitric acid and a few drops of silver nitrate. A white precipitate, insoluble on warming, shows chloride. The concentrated nitric acid is added to prevent the precipitation of silver iodate in case there should still be some iodic acid left in the solution after the treatment with potassium iodide.

If sulphocyanate is present, the test for iodide must be made in a small portion of the solution after addition of sodium acetate. (We add an equal volume of the normal solution of the acetate.) The main portion of the solution is treated as above, the sulphocyanic and hydriodic acids being both completely oxidized in the presence of the acetic acid.

If salts of other acids are present, acidify the solution with dilute nitric acid and precipitate with silver nitrate. Digest the washed precipitate with zinc and dilute sulphuric acid. The halogen acids and sulphocyanic acid are thus brought into solution. Neutralize the solution, filter off the precipitate of zinc hydroxide or carbonate and proceed as directed above.

We have made some comparisons of the delicacy of this method for the detection of chlorides in presence of bromides and iodides with that of the commonly employed chromyl chloride distillation method. The limit of the latter method was found to be the detection of chloride in a mixture of 5 cc. N/100 sodium chloride with 10 cc. N/100 potassium bromide. With such a solution, a very faint yellow ring could be recognized at the top of the liquid (ammonium hydroxide solution) in the receiver. With less than 5 cc. of the sodium chloride solution, we failed to obtain any test

by this method, whereas, using our method, we were able to detect chlorine in mixtures of 0.5 cc. N/100 sodium chloride with 20 cc. of N/5 potassium bromide and iodide. In fact, the results of all our qualitative experiments indicate that absolutely no loss of chlorine is suffered in liberating and expelling the iodine and bromine.

To test the adequacy of the above directions we have had first- and second-year students of the University of Cincinnati analyze some forty mixtures of chlorides, bromides, iodides and sulphocyanates. The solutions were of fifth-normal to normal strength. In the reports there was but a single error, one student reporting chlorine when none was present. Some twenty-five mixtures of more dilute solutions, some containing as low as 0.5 cc. of the N/100 solution of one or other of the halide salts, many containing sulphocyanate and some containing salts of other acids, including reducing agents, such as sulphites, ferrocyanides, oxalates, etc., were analyzed by more experienced persons without error.

Bugarszky[1] has employed potassium biiodate and dilute sulphuric acid for the quantitative separation of bromine and chlorine but has not attempted to separate iodine from the other halogen elements. We hope soon to be able to communicate a method for the estimation of all three elements.

THE TESTING OF COAL TAR AND OILS AND AN IMPROVED TESTING STILL.

By H. W. JAYNE.

Received June 4, 1903.

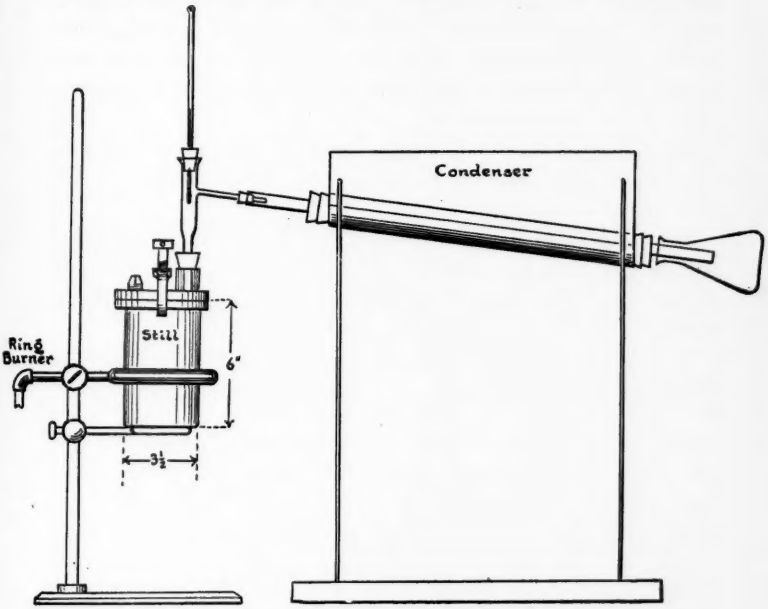
IN the examination of coal tars and oils, and in determining the per cent. of water they contain, it is necessary to distil a considerable quantity of material, from 500 to 1000 cc. at least. In treatises on this subject, it is usual to recommend the use of glass retorts of several liters capacity. As the temperature in making a complete test often rises to 400° C., and as water is usually present, the risk of breakage is very great; and when the distillation is finished, it is impossible to remove the pitch or residue completely.

In our laboratory, where hundreds of these tests are made every

[1] *Ztschr. anorg. Chem.*, **10**, 387 (1895).

year, we found it necessary to substitute a metal still, and, in the course of time, improvements have been suggested by the different chemists making these tests, until a form of still and condenser has been adopted, which will be found convenient for those engaged in this line of work.

The still is of heavy copper with straight sides so that it can be easily and thoroughly cleaned. The upper edge is surrounded



with a heavy turned ring. The lid is of brass, and is clamped to the still by a single clamp passing over the top, a paper gasket being placed between the two metal surfaces. The condenser consists of a copper trough open at the top, through which passes a glass tube 24 inches long. This form of condenser is particularly advantageous for tar distillations. It is filled with water at the beginning of the test, and this is sufficient to condense all the lighter portions. When the fractions containing naphthalene begin to distil, they are liable to choke the tube by the crystallizing of this body. To prevent this, a burner is placed under the trough

and the water warmed to any degree required. When still higher temperatures are reached, where water cannot be used owing to danger of cracking the tube, it can readily be drawn off by the small cock.

In cases where it is necessary to distil very volatile liquids, pieces of ice or a freezing-mixture may be placed in the trough.

For oil-testing, the long Liebig condenser is not advantageous: it is difficult to clean; and on account of its length, considerable material adheres to the sides. As all tests of oils, naphthas and benzenes are run slowly, so that the distillate flows from the condenser in single drops, a long tube and flowing water is unnecessary.

One filling of water will suffice for many tests of benzenes or oils. If, however, flowing water is needed, the condenser is fitted with connections for tubing.

For water determinations, a small still is used of a capacity of 1000 cc. sufficient for distilling 500 cc. of tar. For complete tests of tars, especially if the light oils are to be examined, 1000 cc. should be used, and the still has a total capacity of 2000 cc.

For water determinations, great care must be taken in collecting the sample. If the shipment is made in bulk, a small cock should be placed in the pipe line from the car or boat to the tanks, and a small stream allowed to flow during the entire pumping. The quantity so collected should be violently stirred, and at once filled into wide-mouthed quart bottles or cans before any separation can take place. 500 cc. of this sample are filled into the still, the lid securely clamped, and the tube and thermometer put in place. If heat is applied to the bottom of the still, great care must be used, as the contents will readily foam and boil over, if much water is present; this is especially true of tars containing much free carbon along with water, and also of certain oil tars in which the water forms an emulsion.

To avoid this, a ring burner is provided which surrounds the still, and is at first placed so that the heat strikes about the top of the tar in the still. Little attention need be given the distillation but from time to time the ring burner is lowered, until finally nearly all the water is driven out, when, if necessary, an additional burner is placed under the bottom.

In order to be certain that all water is expelled, the temperature of the thermometer in the vapor should reach 200° C. As the distillation proceeds, oil comes over with the water until at 200° a considerable quantity of the former has distilled. The volume of the water is then read off in cubic centimeters, and gives the volume per cent., on which all these tests are based.

If, after the water has been determined, it is desired to examine the tar or oil further, the oil which has distilled over with the water is carefully separated from the latter and added to the cooled tar in the still, and the distillation recommenced; thus, the subsequent determination will be based on dry tar. Unless this is done, false results are obtained, due to the oils distilling at lower temperatures in the presence of vapor of water. For example, a tar, which, if dry, would show 5 per cent. distilling under 200° C., might show 20 per cent. to the same point if much water was present.

The ring burner may be dispensed with during this latter distillation, and it is advisable to cover the still with a sheet of asbestos, if a high temperature is to be finally reached.

If at any time it is desired to examine the material in the still, this can be done without dismounting the apparatus by removing the small plug in the lid, and introducing a rod. The pitch or residue can be tested as to the melting-point or other properties, and if not of the desired test, the distillation can be continued.

Some tars are exceedingly difficult to free from water, the contents of the still boiling over notwithstanding all precautions. If it is desired to determine only the water in these, the removal of the latter can be greatly facilitated by adding to the tar a hydrocarbon, boiling slightly higher than water—crude or refined toluene, for instance. This thins the tar, and as it distils readily, carries over the water completely. Distillations which otherwise would require hours to complete, can be then readily made in twenty minutes.

This method is also very advantageous for determining water in naphthalene or oils rich in this substance, as it facilitates the driving out of the last traces of water, and prevents crystallizing of the naphthalene in the condenser tube and receiver, and permits the volume of water to be readily read off.

In these determinations a pure product need not be used—any hydrocarbon boiling between 100° and 200° will serve, the precaution being taken, however, to determine how much water it contains, and allowing for the same.

Recently a German patent No. 130,295 was granted for determining water in substances by adding a higher boiling liquid than water and one that does not mix with it. It is to be regretted that these simple laboratory methods should be made the subjects of patents, and it is difficult to understand the object of taking such a patent; but in this case it would be invalid in the United States, as the method has been used for a long time at different works.

LABORATORY, BARRETT MANUFACTURING CO.

A PROCESS FOR MAKING AVAILABLE PHOSPHATES.

BY C. H. DEMPWOLF, JR.

Received May 29, 1903.

A NUMBER of processes for the manufacture of available phosphates by means other than that of sulphuric acid have been recently proposed. From among these processes the following have been taken as seeming of the most importance.

G. F. Wilson (1861) patented a process, which consists in treating ground mineral phosphates, bone-black, etc., with fused sodium bisulphate and steam under high pressure. A double decomposition of the tricalcium phosphate into calcium sulphate and sodium phosphate is claimed for the process, thus leaving the phosphoric acid in a form more available as a plant food. The source of the bisulphate is the waste product obtained in the manufacture of sulphuric and hydrochloric acids.[1]

G. A. Liebig (1881) proposed a process in which phosphates are mixed with carbon and subjected to a high heat. The proportions given are two parts of the phosphate to one of carbon.[2]

The process of Brunner and Zanner consists in treating the finely powdered natural phosphates with a solution of sodium bisulphate. After filtration, the liquid contains the calcium acid phosphate, which is then precipitated by an excess of lime.[3]

[1] U. S. Patent 75,325.
[2] U. S. Patent 241,868.
[3] *Moniteur Scientifique*, 1892, p. 100, and Eng. Patent 2,389, Feb. 8, 1892.

A method of making hydrated phosphate of alumina soluble in ammonium citrate was proposed by Pillon Freres and Buffet in 1892. This process is simply a dehydration by the action of heat and is used in the manufacture of Redonda phosphate.[1]

Stephen L. Goodale obtained a United States patent on a similar process in 1893. Morse has shown, however, that the dehydrated phosphate of alumina, as sold under the name of Redonda phosphate, absorbs water very rapidly and reverts to the hydrated or insoluble form, this being its probable action in the soil.[2]

C. H. Knoop, by heating mixtures of natural phosphates with alkaline silicates or materials capable of forming these silicates, to a red heat, obtained a complex alkaline phosphate, in which 99 per cent. of the phosphoric acid is soluble in Wagner's citrate solution. The following charges are given as yielding good results:[3]

	Parts.
Tricalcium phosphate	100
Calcium carbonate	80
Sodium sulphate	60
Silica	54
Tricalcium phosphate	100
Calcium carbonate	36
Magnesium sulphate	185
Silica	54

J. G. Wiborgh, of Stockholm, obtained a patent in the United States on a process of igniting apatite with alkaline carbonates or hydroxides. It consists in pulverizing the apatite and mixing it with carbonate of sodium or potassium or with sodium or potassium hydroxides, and subsequently heating the mixture to a red or yellow heat. A tetracalcium sodium (or potassium) phosphate is formed according to the following equation:

$$3Ca_3(PO_4)_2.CaF_2 + 3Na_2CO_3 = Ca_{10}Na_4P_6O_{27} + 2NaF + 3Co_2$$

This double phosphate is readily soluble in ammonium citrate.[4]

A more recent patent of Wiborgh and Palmaer (1903) describes an electrolytic process for the manufacture of soluble phosphates. Apatite or other phosphate is placed in an electrolytic cell with a salt solution adapted to liberate an acid at the anode, forming a soluble salt with lime, while at the cathode a basic hydroxide is

[1] *Moniteur Scientifique*, 1892, p. 210, and Eng. Patent 6,023, Nov. 30, 1892.
[2] This Journal, 1903, p. 280.
[3] *Centralblatt*, 1899, p. 1052.
[4] U. S. Patent 601,089.

formed, the acid dissolving the phosphate and precipitating the same in the alkaline liquid of the cathode.[1]

Shutt, in a paper on the action of ground mineral phosphates as a fertilizer,[2] describes experiments on the fusion of apatite with sodium sulphate and sodium bisulphate. It was found that when apatite is fused with sodium sulphate, 35 per cent. of the total phosphoric acid in the product becomes soluble in a 2 per cent. citric acid solution. When the bisulphate is used, 50 per cent. of the total phosphoric acid is soluble.

The use of a 1 per cent. citric acid solution as a means of determining the availability of phosphates as a plant food is customary in England. The results obtained by Shutt are probably higher than would be given by a 1 per cent. citric acid solution or the neutral solution of ammonium citrate, as adopted by the Association of Official Agricultural Chemists.

Baskerville noted that when natural phosphates were heated with alkaline salts, such as sodium sulphide, sodium nitrate, sodium carbonate and sodium sulphate, a large proportion of the phosphoric acid became citrate-soluble. The rock contained 35 per cent. $Ca_3(PO_4)_2$ and was mixed with sodium carbonate in the proportion of 4 of rock to 1 of carbonate. The mixture was heated to a red heat and gave a 75 to 90 per cent. yield, depending upon the temperature and the duration of heating. The percentage of water-soluble phosphoric acid was not notably increased.[3]

EXPERIMENTAL.

This work was undertaken with a view to the utilization of niter cake, the by-product from the manufacture of sulphuric acid, and at the same time the production of an available phosphate. This niter cake is the residue from the treatment of sodium nitrate with sulphuric acid and is composed mainly of sodium bisulphate with a small percentage of the normal sulphate. The niter cake used in these experiments was found to contain $NaHSO_4$, 86.93 per cent.; Na_2SO_4, 9.72 per cent.

EXPERIMENTS WITH BONE ASH.

Twenty grams of ground bone-ash containing 40.16 per cent. insoluble phosphoric acid was mixed with an equal quantity of niter cake and heated in a porcelain crucible for thirty minutes

[1] U. S. Patent 707,886 and this Journal, 1903.
[2] *Chem. News* (1896), p. 4.
[3] *J. Soc. Chem. Ind.*, December, 1902.

with the blast-lamp. The mixture before heating contained 20.08 per cent. phosphoric acid. A second charge was run at the same time, using 20 grams bone-ash, and 20 grams niter cake, with the addition of 4 grams charcoal. This mixture was heated for the same length of time and at the same temperature as in the first case.

The analyses of the sintered masses may be stated as follows:[1]

Charges.	20 grams bone-ash. 20 grams niter cake.	20 grams bone-ash. 20 grams niter cake. 4 grams carbon.
Water-soluble P_2O_5	0.13	3.70
Citrate-soluble P_2O_5	2.66	14.16
Insoluble P_2O_5	18.30	6.59
Total P_2O_5	20.99	24.45
Ratio of available P_2O_5 to total P_2O_5	13.24	73.05

This increase in the percentage of available phosphoric acid is due mainly to the formation of the double phosphate of calcium and sodium ($Ca_{10}Na_4P_6O_{27}$), which is soluble in ammonium citrate solution and to a slight extent to the fact that tricalcium phosphate is more soluble in water containing alkaline salts than in pure water. Other double phosphates of calcium and sodium have been prepared, and Baer mentions a calcium sodium pyrophosphate having the formula $CaNa_2P_2O_7.4H_2O$.[2] The formula as given by Wiborgh corresponds to the tetracalcium phosphate as present in basic or Thomas slag and is probably the one which is formed under these conditions.

The analyses show that when carbon was used, the ratio of available phosphoric acid to total phosphoric acid was increased from 13.24 to 73.05 per cent. The sodium bisulphate was used in excess over the amount necessary to form the double salt $Ca_{10}Na_4P_6O_{27}$, while the carbon used was the calculated amount necessary to reduce the sodium acid sulphate to sodium sulphide. When sodium bisulphate is heated, it loses water according to the equation

$$2NaHSO_4 = Na_2S_2O_7 + H_2O.$$

This pyrosulphate, at a somewhat higher temperature, loses sulphur trioxide and the normal sulphate is formed,

$$Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

[1] The methods of analysis used in these experiments were those adopted by the Association of Official Agricultural Chemists and described in Wiley's "Principles and Practice of Agricultural Analysis," Vol. II.

[2] Pogg. *Ann.*, **75**, p. 159.

The action of the carbon is to reduce the normal sulphate thus formed to sodium sulphide according to the following reaction:

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

It is probable that some polysulphides are also formed.

EXPERIMENTS WITH PHOSPHATE ROCK.

Similar experiments were made, using a natural Florida phosphate containing 30.28 per cent. P_2O_5, of which 1.30 per cent. was citrate-soluble. These charges were heated exactly as in the preceding case and yielded the following analyses:

Charges.	20 grams rock. 20 grams niter cake.	20 grams rock. 20 grams niter cake. 4 grams carbon.
Water-soluble P_2O_5	0.38	0.27
Citrate-soluble P_2O_5	5.12	8.87
Insoluble P_2O_5	13.89	11.55
Total P_2O_5	19.39	20.69
Ratio of available P_2O_5 in total P_2O_5	28.36	44.17

Here the increase in yield, due to the action of the carbon in forming sodium sulphide, is not so large as when bone-ash was used.

The effect of heat alone upon the phosphate rock was determined by igniting 20 grams of the rock for thirty minutes in the blast. The analysis, after ignition, shows a small increase of citrate-soluble phosphoric acid, due probably to the dehydration of the ferric and aluminum phosphates present.

	Analysis of rock before ignition.	Analysis of rock after ignition.
Total P_2O_5	30.28	31.82
Citrate-soluble P_2O_5	1.30	3.27

A mixture of 10 grams phosphate rock and 10 grams sodium sulphide, heated as described above, gave the following analysis:

Water-soluble P_2O_5	0.18
Citrate-soluble P_2O_5	11.32
Insoluble P_2O_5	8.86
Total P_2O_5	20.36
Ratio of available P_2O_5 to total P_2O_5	56.43

It was believed that the above results could be improved upon, and the following experiments were made in order to determine the effect of temperature, duration of heating and the proportion of ingredients in the mixture upon the amount of available phosphoric acid in the product.

In order to determine the most effective temperature, mixtures of 10 grams phosphate rock, 10 grams niter cake and 2 grams charcoal were heated for thirty minutes at temperatures of 830°, 1090° and 1200° C. and for one hour at 830° and 1090° C. The analysis of the products are shown in the following table:

	30 minutes.			1 hour.	
Temperature	830°	1090°	1200°	830°	1090°
Water-soluble P_2O_5	0.16	0.33	0.24	0.30	0.25
Citrate-soluble P_2O_5	8.26	10.00	12.55	8.19	13.57
Insoluble P_2O_5	11.83	9.54	8.77	12.05	7.33
Total P_2O_5	20.25	19.87	21.56	20.54	21.15
Ratio of available P_2O_5 to total P_2O_5	41.58	51.98	59.32	41.33	65.34

These results indicate that the amount of available phosphoric acid is increased by an increase in temperature and duration of heating. The charges heated to 830° and 1090° were very porous and easily pulverized, while the charge heated to 1200° for thirty minutes was partly fused and difficult to break.

Mixtures containing 10 grams phosphate rock and varying proportions of 4, 6, 8 and 10 grams niter cake, with carbon sufficient in each case to reduce the bisulphate, were made up and heated for one hour at a temperature of 1090° C. The results of the analyses of these products are as follows:

	10 grams rock. 4 grams niter cake. 0.8 gram carbon.	10 grams rock. 6 grams niter cake. 1.2 grams carbon.	10 grams rock. 8 grams niter cake. 1.6 grams carbon.	10 grams rock. 10 grams niter cake. 2 grams carbon.
Water-soluble P_2O_5	0.12	0.19	0.28	0.25
Citrate-soluble P_2O_5	16.53	15.74	12.53	13.57
Insoluble P_2O_5	10.84	9.13	8.96	7.33
Total P_2O_5	27.49	25.06	21.77	21.15
Ratio of available P_2O_5 to total P_2O_5	60.56	63.56	58.84	65.34

The differences shown above between the ratios of available phosphoric acid to total phosphoric acid are not very great, the best yield being obtained with the mixture containing 10, 10 and 2 parts respectively of rock, niter cake and carbon. The product from this charge contained considerable excess of sodium sulphide, which, on exposure to air, oxidized to sulphate and absorbed water very rapidly. One gram of this phosphate was exposed under a bell-jar for several days to an atmosphere saturated

with moisture. The increase in weight due to oxidation and absorption of water was noted as follows: After 24 hours, 0.1856 gram; after 48 hours, 0.2148 gram; after 72 hours, 0.2254 gram.

One gram of the phosphate from the mixture 10 grams rock, 4 grams niter cake and 0.8 gram carbon was exposed in a similar manner, the absorption in this case being considerably less than the above figures. The increase in weight for three days was after 24 hours, 0.0384 gram; after 48 hours, 0.0522 gram; after 72 hours, 0.0550 gram.

A modification of Knoop's charge, using a proportional quantity of niter cake in place of the normal sodium sulphate, was tried, but with little success. The charge was made up by mixing 20 grams phosphate rock, 10.6 grams calcium carbonate, 16 grams niter cake and 6.6 grams silica, and heated for a half hour at a temperature of 1090° C.

Analysis:

Water-soluble P_2O_5	...
Citrate-soluble P_2O_5	0.80
Insoluble P_2O_5	12.31
Total P_2O_5	13.11
Ratio of available P_2O_5 to total P_2O_5	6.10

A double phosphate and silicate of lime corresponding to the formula $Ca_3(PO_4)_2.CaSiO_4$ would be formed under these conditions and does not seem to be soluble to any great extent in the neutral citrate of ammonia.

A method of treating the phosphate rock with the niter cake in solution was more successful than any of the above-described experiments. Twenty grams of the ground rock and twenty grams of niter cake were mixed in a beaker-glass and water added to form a thin paste. This was allowed to stand for four weeks with frequent addition of water and stirring, at the end of which time the water was allowed to evaporate and the mixture dried in the air. An analysis of the product thus obtained was as follows:

Water-soluble P_2O_5	6.89
Citrate-soluble P_2O_5	...
Insoluble P_2O_5	5.54
Total P_2O_5	12.43
Ratio of available P_2O_5 to total P_2O_5	55.43

In this case no citrate-soluble phosphoric acid was formed, all of the available phosphate being soluble in water. The tricalcium phosphate, being somewhat soluble in water containing alkaline salts, neutralizes the acidity of the bisulphate according to the equation

$$Ca_3(PO_4)_2 + 4NaHSO_4 = CaH_4(PO_4)_2 + 2Na_2SO_4 + CaSO_4.$$[1]

CONCLUSIONS.

The sulphuric acid industry being so closely allied to the manufacture of fertilizers, it would seem from the foregoing work that it is possible to utilize the sodium bisulphate, niter cake, to good effect in the production of an available phosphate. The cost of producing acid phosphate on a large scale by means of sulphuric acid is very low and any process, even though an auxiliary one, for the production of the same phosphate must necessarily be a cheap one.[2] The method of heating mixtures of niter cake, phosphate rock and carbon would probably be more expensive than the present one for any but a cheap low-grade phosphate rock. Furthermore, there is a general prejudice against the use of citrate-soluble or so-called "reverted phosphoric acid", although it has been given the same value as that soluble in water by the various experiment stations of this country.

It is believed by agricultural chemists that when an acid phosphate, containing the various forms of phosphoric acid is applied to a soil containing iron and alumina, the soluble parts of the compound tend to become fixed by union with such bases or by precipitation as $Ca_2H_2(PO_4)_2$.[3]

The method of treating the pulverized phosphate with a solution of niter cake promises to be more successful, since the available phosphoric acid in the product constitutes 55.43 per cent. of the total phosphoric acid and is completely soluble in water. By finer grinding of the rock, it may be possible to increase the yield, and the time four weeks may be longer than is necessary to complete the reaction.

[1] It is possible that some sodium phosphate may be formed in the above process.
[2] A 14 per cent. acid phosphate can be made for about $7 per ton.
[3] Wiley's "Principles and Practice of Agricultural Chemical Analysis," Vol. II., p. 140.

A PRELIMINARY REPORT UPON THE OXIDATION OF LINSEED OIL.

By Frederick L. Dunlap and Francis D. Shenk.

Received May 21, 1903.

The question of the phenomenon of the drying of linseed oil is one of great interest, but while more or less work has been done on this subject, in order to elucidate the chemical changes taking place during the drying of linseed as well as other drying oils, yet our knowledge of the subject is far from complete. We undertook this work with the hope of being able to throw more light on this question, but the fact that we are unable to further carry on this work in conjunction, makes it necessary that this report should be considered merely in the light of a preliminary one, and it is hoped that later, one of us may be able to fill in the gaps that are lacking in the experimental part of this report.

The first work of importance on the subject of the chemistry of drying oils, with reference to the action of air on them, is in the classic work of Mulder,[1] although previous to Mulder, Unverdorben[2] and Leuchs[3] had made a brief study of the action of air on linseed oil, but their results were not such as to lead to any definite conclusions.

Mulder's work on the chemistry of the drying oils, was published in German in 1867, and included in it the results of his researches on the action of air on linseed oil as well as on the free acids of linseed oil. At the time when Mulder carried on his researches, the knowledge of the constitution of these oils was very incomplete, nor was much known about them until the publication of the beautiful researches of Hazura and others in the *Monatshefte*.[4] Mulder came to the conclusion that the liquid acids in linseed oil contained besides oleïc acid, an acid of the composition $C_{16}H_{28}O_2$ (leinölsäure). On oxidation of linseed oil by means of air, Mulder held that the glycerin was completely oxidized, that the free fatty acids and the greater part of the oleïc acid remained unchanged, and that the acid $C_{16}H_{28}O_2$ at first formed the acid $C_{16}H_{26}O_5$ (linoxysäure) and finally as an end-product of the oxidation, the neutral linoxyn $C_{32}H_{54}O_{11}$.

[1] "Chemie der austrocknenden Oele." Translated from the Dutch by J. Müller. Berlin, 1867. Julius Springer.

[2] Schweigger's *Jour.*, **17**, 245.

[3] Gmelin-Kraut, **7**, 1231.

[4] **7**, 216; **8**, 147, 156, 260; **9**, 180, 198, 475.

Hazura[1] has shown as the results of his study of the action of potassium permanganate on an alkaline solution of the liquid acids of linseed oil, that linseed oil contains the glycerides of the following acids: Oleïc, $C_{18}H_{34}O_2$; Linolic, $C_{18}H_{32}O_2$; Linolenic, $C_{18}H_{30}O_2$; Isolinolenic, $C_{18}H_{30}O_2$. It was impossible that Mulder should have been able to come to any correct conclusion on the oxidation of linseed oil by means of air, for from the work of Hazura we can see that Mulder was dealing with a more complicated product than he was aware of, and that,[2] for example, his linoxy acid, $C_{16}H_{26}O_3$, obtained from the acid $C_{16}H_{28}O_2$, could not have been the simple product that Mulder took it to be, but must have been a mixture of products, which furthermore could not have contained an acid of the chain C_{16}, but must have been those of the higher chain C_{18}.

Bauer and Hazura[3] studied the phenomenon of the drying of oils, and have clearly shown that the results obtained by Mulder on his linoxy acid are unreliable. So far as the action of air is concerned, Bauer and Hazura studied its action on the free acids of linseed oil, on the barium and lead salts, and on the linseed oil itself. In brief, their conclusions are as follows: The oleïc acid undergoes no change whatsoever; the more linolenic acid there is in the oil, the more rapidly it dries; the oxidation consists not only in the saturation of the free valencies with oxygen, but also in the formation of compounds containing hydroxyl groups; the acids dry, on long exposure to the air, with the formation of anhydrides, but that they were unable to say whether such anhydrides were lactonic in nature or formed from 2 molecules of the oxyacids; and finally, that there is no difference between the drying of the free acids and their salts.

For some not very well-defined reason, Bauer and Hazura concluded that as they had shown clearly the constitution of the unsaturated acids in linseed oil, it appeared "unnecessary to isolate the individual compounds from the oxidation product obtained from the acids of linseed oil by the action of air upon them; it is sufficient to show in what way the oxidation takes place." In this, we can not agree with Bauer and Hazura that all that is necessary is to show in what way the oxidation takes place, unless

[1] *Monatsh. Chem.*, **9**, 191 (1888).
[2] *Ibid.*, **9**, 460 (1888).
[3] *Ibid.*, p. 459, *et seq.*

in so doing, it is perfectly evident what the final products of such an oxidation may be. In order to elucidate the chemical changes taking place when linseed and other oils dry, either the individual oxidation products must be isolated and analyzed, or else, if this prove impracticable, results must be obtained from some other but less direct route. None of the experimental results of Bauer and Hazura can be interpreted to mean that the oxidation by air gives rise to the same products as are obtained by the action of potassium permanganate on an alkaline solution of the linseed oil acids. Nor are the conclusions of Bauer and Hazura as given above, namely, with reference to the formation of hydroxy acids and anhydrides, etc., given with sufficient definiteness to help us to anything like a clear understanding of the question. We have spent considerable time in attempts to isolate some of the hydroxy acids described by Hazura[1] as resulting from the action of potassium permanganate on the unsaturated acids of linseed oil, but, in the product obtained from the action of air on linseed oil, we have been unable to obtain a trace of any product resembling those obtained by Hazura with potassium permanganate, nor is there any *a priori* reason for believing that the oxidation would follow the same lines. We judge from the context of the article of Bauer and Hazura that they wish to convey the idea that air and potassium permanganate produce identical results in the oxidation in question, otherwise we are at a loss to understand why they deem it unnecessary to isolate the oxidation products, but think it sufficient to dismiss the question with a few conclusions quoted at the beginning of this paper.

In 1893, Fahrion[2] published an article on the oxidation of oils by means of air, in which work he gives the results of some oxidation products which he isolated and subjected to analysis. He oxidized linseed oil, for example, by saturating chamois skin with the oil and allowing the skin so treated to hang in the air until the oxidation was finished. But Fahrion himself shows that he had not obtained pure products, but only mixtures of various oxy-acids.

The above references to the literature give, so far as we have found, the results bearing directly on the chemical changes taking place during the drying of linseed oil.

[1] *Monatsh. Chem.*, **9**, 191 (1888).
[2] *Chem. Ztg.*, **17** (2), 1849 (1893).

We have attacked the problem in two ways, first, the oxidation of linseed oil when dissolved in ligroïn; and second, when dissolved in benzene. A reference to the action of air on linseed oil, when dissolved in benzene, occurs in Allen's "Commercial Organic Analysis."[1] Whether this work is abstracted from a published article or is the result of some experiments carried out by Allen himself, we cannot say, but we have found no trace of any suggestion regarding the oxidation of linseed oil in benzene solution other than that given by Allen. The few lines devoted by Allen to this subject, do not contain any results which cast any light on the chemical side of this phenomenon of oxidation.

The serious objection to the oxidation of linseed oil by spreading it in thin layers on metal or glass plates, and then exposing them to the air, either at ordinary or elevated temperatures, is that it is a process that may take weeks or even months of exposure in order to bring about thorough oxidation, and even then it is a serious question whether or not the oxidation has become complete. As soon as the superficial layer of the oil becomes coated with a layer or film of the oxidized product, the oil lying below this film, and which is unacted upon by the air, is more or less effectively removed from the action of the air by the film on the surface. This latter objection is also applicable to Fahrion's scheme of oxidizing linseed oil which has been exposed to the air on chamois skin.

By dissolving the linseed oil in a suitable solvent, and then aspirating air through it, the above objections are readily overcome. Low-boiling ligroïn and benzene serve admirably for this purpose.

The sample of linseed oils used for the experimental part of this work, was a sample of pure boiled oil containing lead and manganese as driers. The iodine number, acid value, etc., of this oil, are given at the beginning of the table later on in this article.

To determine the rate of oxidation, 100 grams of the boiled oil were dissolved in 1,000 cc. of ligroin (boiling-point below 90°) and air drawn through the solution. This was started November 10th. After forty-eight hours, the oxidation product that had separated was filtered off, thoroughly macerated with ligroïn, then

[1] Third edition, Vol. II, Part I, p. 152.

washed several times with a lower boiling product to remove any of the original linseed oil mechanically held. After drying first in air then *in vacuo* over sulphuric acid, a sharp odor was given off similar to that of hydrochloric acid, only stronger, and resembled the odor of acroleïn. This solid oxidation product weighed 17.5 grams. Air was again drawn through the ligroïn solution and after forty-eight hours more, a second batch was filtered off. This also had the sharp odor noted above. This lot weighed 24 grams. A third lot was taken out November 16th ; weight, 25 grams. It did not have the sharp odor—was white and almost transparent. The fourth and last batch was filtered off four days later; it weighed about 15 grams and looked the same as the third lot. Air was again drawn through the solution until November 24th, and as no product had separated since the last filtering, it was sufficient evidence that the oxidation was complete November 20th or before. The total weight of products was 81.5 grams. The remaining solution was clear but fluorescent while cold, and upon distilling off the ligroïn *in vacuo,* the fluorescence disappeared and a precipitate formed. Weight of final product was 20 grams. The ligroïn that distilled off had a very sharp penetrating odor like that previously mentioned in connection with the first oxidation products. After standing for a couple of weeks, the sharp odor entirely disappeared from the ligroïn. About 5 grams of the last product was solid, the rest a deep yellow oil. The first oxidation products that separated were darker in color than those separated later. During the aspirating of air through the ligroïn solution of the linseed oil, the ligroïn lost by evaporation was replaced by fresh solvent so that the volume remained practically constant.

Since the oxidized oil seemed to form two distinct products, so far as color was concerned, an experiment was run to determine whether there was any special difference between them. This was started in the same way as the above experiment, but the oxidation product was allowed to collect until the oxidation was complete. A mechanical separation was then made of these two layers. The dark layer, called A, and the light layer, called B, were each subjected to the method of washing previously mentioned. Each layer weighed approximately 60 grams. They were then sub-

jected to repeated extractions with boiling ether until no residue remained on evaporating the solvent. The ether extract from A (A_1) weighed 20 grams, while that from B (B_1) weighed 30. As will be seen from the following table, there is a slight difference in the iodine numbers of the ether-soluble and the ether-insoluble portions of the product A. The part A carried more of the manganese of the dryer than the part B.

The ether insoluble of B was extracted several times with large quantities of boiling chloroform. Out of 31 grams taken, only 28 grams were dissolved by the chloroform; this, after evaporating off the solvent, was of a reddish brown color, but gradually turned white on standing. The part insoluble in chloroform was a grayish white product of a rubbery consistency. According to Mulder[1] the oxidation product is dissolved by a mixture of alcohol and chloroform, but the products we obtained were not, if conclusions can be drawn from the following experiment. Four-tenths of a gram of the ether-insoluble portion was heated to boiling for sixty hours in a mixture of 400 cc. of alcohol and chloroform, one part of the former to four of the latter. At the end of that time a considerable portion was still undissolved. When heated with alcohol and chloroform, the product does swell, but the swelling is due to the chloroform alone, not to the alcohol. It also swells slightly when heated with ether and can be easily ground to a fine powder after the ether is poured off.

On December 5th another sample of 100 grams of the oil was oxidized as the above, but benzene was used instead of ligroïn. At first, no product separated as from the ligroïn solution. At the end of eighteen days the oil had an iodine number of 37; by January 15th the iodine number was 24.9. By February 1st a solid product had separated out; this was filtered off and washed several times with benzene. The dry product, called C, weighed 18 grams. Air was again drawn through the remaining oil for a month more, but nothing further separated. After filtering off the solid product, the oil had an iodine number of 35, and the lowest we were able to get it after that was 31. Twenty-two per cent. of the above solid product was soluble in ether, which shows that the product may differ to a certain extent from that separating from the

[1] "Chemie der Austrocknenden Oele," p. 98.

ligroïn, as the ether-soluble part of the product separating from ligroïn was nearly 50 per cent. of the total solid.

In determining the iodine number, the various samples had to be heated to the temperature of the water-bath in order to effect solution (except in the case of the ether-soluble). When this had been accomplished, Wiji's solution of ICl in glacial acetic acid was added and allowed to stand for lengths of time varying from fifteen minutes to nearly an hour. In general, the iodine absorption was found to be complete in twenty-five to thirty-five minutes, *i. e.*, for a shorter time the iodine absorption was low and increased to a constant when allowed to stand for the period just indicated.

The dissolving of the oxidation product in glacial acetic acid, by means of heat, produced a solution of slightly reddish color. Where, for example, the product was soluble on long shaking with glacial acetic acid at ordinary temperatures, as were the ether-soluble products A_1, B_1 and C_1, the iodine absorption was found to be less than when such solution was effected by means of heat. For the ether-soluble products A_1, B_1 and C_1, solution was effected by means of automatic shaking for periods varying from three to ten hours, and in the following table the iodine numbers given represent the results of solution produced without the aid of heat.

A_2 and B_2 were nearly all soluble in cold glacial acetic acid and it is highly probable that they are completely soluble if sufficient acid is used, but we were unable to carry out this work for lack of time.

A_1, B_1 and C_1 were all thick, viscous, yellowish oils, which on long standing in the air grew more viscous, becoming coated with a film like that forming on linseed oil itself. A_2, B_2 and C_2 were of a leathery or gutta percha-like consistency.

In determining the iodine numbers, Wiji's method was used throughout, as Hübl's method could not be used, for glacial acetic acid was found to be the only satisfactory solvent for these products.

The following table gives some of the results obtained from the various oxidation products.

Substance.	Iodine number.	Acid value of potassium hydroxide. Milligrams.	Saponification value of potassium hydroxide. Milligrams.	Ether value.
Original oil	176.6	4.00	183.0	177.8
	176.9	4.00	180.6	....
A	44.8 (?)	...	....	....
	54.2	...	....	....
B	26.7	...	....	....
	28.5	...	....	....
C	22.0	...	....	....
	22.7	...	....	....
A_1, soluble in ether	54.9	64.5	251.7	190.2
	54.2	64.7	258.0	....
B_1, soluble in ether	42.2	66.5	237.2	171.4
	42.1	67.0	239.1	....
C_1, soluble in ether	25.4	98.2	330.0	230.4
	25.4	101.1	....	....
A_2, insoluble in ether	32.5	...	....	....
	34.8	...	....	....
B_2, $CHCl_3$ extract of ether-insol.	32.2	71.2[1]	321.1	243.3
	32.9	85.7[1]	322.3	....
C_2, insoluble in ether	24.2	...	....	....
	24.7	...	....	....
B_3, insoluble in ether or $CHCl_3$	28.6	...	....	....
	29.1	...	....	....
Oil not precipitated from ligroïn	65.0	21.6	193.1	171.4
	66.0	21.7	193.9	....
Acids from ether-soluble. (B_1)	51.8	231.2	268.9	37.7
	52.9	231.5	269.6	...
Acids from ether-insoluble. (B)	43.4	265.2	307.0	42.4
	45.9	265.8	309.0	...

The ether value was obtained by taking the difference between the mean of the saponification values and the mean of the acid values.

From the free fatty acids of A_1, B_1 and C_1 white crystalline products were obtained. Crystalline products of a similar nature were obtained from the ether-insoluble portion. To show that this product did not come from any of the original oil carried down mechanically by the oxidation product, 25 grams of the oxidized oil were heated with ether, which rendered the product very brittle, and it was then finely ground. This was then extracted with ether in a Soxhlet extractor for ten hours, which removed all of the original oil and also all of the oxidized part soluble in ether. When

[1] These figures do not represent the true acid value, as we found it impossible to bring the last traces of this product into solution, before titrating with potassium hydroxide.

the product was dried after the extraction, it was of the consistency of cornmeal, and absolutely free from sticky material. It required not over fifteen minutes for complete saponification with a 25 per cent. potassium hydroxide solution; sufficient heat was generated by the reaction itself to effect the result. The fatty acids were thrown out with sulphuric acid and the solution cooled with ice so the acids could be lifted out in a lump with a stirring rod; without cooling, the acids could not be separated from the water by mechanical means. They were then thoroughly washed with water and dried; the weight was 15.2 grams. After mixing with quartz sand, the acids were extracted with ligroïn. The weight of product extracted was 1.2 grams. This was perfectly white and was crystallized from glacial acetic acid. The part insoluble in ligroïn was then extracted with ether. The ether extract weighed 10 grams; that insoluble in ether weighed nearly 4 grams and was very dark in color.

By fractional crystallization, 1.2 grams of the white crystalline product were separated into two products melting at 60°-61° and 52°-53°. This required a large number of fractions to be made, and at the end of this work but very small amounts of the two products were obtained. We are disposed to think that these two products are respectively palmitic and myristic acids, although it is difficult to understand how these acids could have been present in the product from which they were obtained, for, as pointed out above, this product had been extracted for ten hours with ether.

The fact that the benzene solution of linseed oil could not be brought to have a lower iodine number than 31 by continued aspiration of air through the solution, shows conclusively that the products of which linseed oil is composed can not be completely oxidized by air. From what is known of oleïc acid and its properties, there is no reason to doubt but that the iodine number was produced, at least in part, from the unchanged oleïc acid or oleïn. This, however, is but in agreement with the well-known fact that oleïc acid is practically unacted upon by the oxygen of the air. From the large increase in the acid value, it is evident that the oxidation of linseed oil by air takes place to a considerable extent through the oxidation of the glycerin of the glycerides. While we have been unable, for lack of time, to attempt an isolation of the product having the sharp, characteristic odor of acroleïn, yet

it is not impossible that acroleïn may be formed during this progress of oxidation. That the air oxidizes linseed oil with the formation of carbon dioxide, formic and acetic acids, has been shown by Mulder[1], from which we can see that the chemical changes taking place during the drying of the glycerides are complex. That the acroleïn-like odor came from the linseed oil and not from the ligroïn, was determined by a blank experiment. It is also evident that the oxidation in ligroïn by means of air gives rise to products that are still unsaturated. While no acetyl values were determined, yet it was sufficiently well shown by Hazura[2] that products containing the hydroxyl group are formed. That we were, for example, dealing with a product free from any unoxidized oil or free oleïc acid, let us consider such a product as B_2 or C_2. If any unoxidized oil was carried down mechanically with the oxidized product, it must have been in small quantities. If any such occluded oil or free oleïc acid were present, it must have been completely removed by the subsequent maceration and washing of the product with ligroïn, and in the long and thorough extraction with ether. Even after such treatment, the iodine number of C_2 was found to be 24.5 (mean value), while in the case of B_2 it was 33.6 (mean value), and in B_3 it was 28.9 (mean value). From this we must conclude that the oxidized product thrown out from a ligroïn solution is an unsaturated hydroxylated product.

What the exact chemical nature of these products is, it is, at present, impossible to say; nor can we, as yet, be assured that the product obtained from ligroïn is identical with the product obtained by oxidation without a solvent. Bauer and Hazura[3] obtained, by Hübl's method, an iodine number of 28.8 and 29.4 for the free acids obtained from linoxyn. We obtained an iodine number of 43.4 and 45.9 from our corresponding product, *i. e.*, the free acids of the ether-insoluble portion.

The ether values 37.7 and 42.4, obtained from the acids of the ether-soluble and ether-insoluble products, point to the presence of lactones in the acids, and it is altogether probable that lactones are also present in the other products given in the table, and that the ether values do not represent alone the amount of glycerin in

[1] "Chemie der Austrocknenden Oele," p. 109.
[2] *Monatsh. Chem.*, **9**, 462 and 463 (1888).
[3] *Ibid.*, p. 467.

these unsaponified products, but also the lactones present. Lekowitsch,[1] in an article "On Oxidized Oils," points out the probable presence of lactones in solidified linseed oil (linoleum mass) through the difference in the acid and saponification values from the free acids.

The question has arisen whether or not the product with which we worked, which was insoluble in ether, was identical with Mulder's linoxyn. So far as characteristics are concerned, our ether-insoluble product was identical, except that Mulder says that linoxyn is insoluble in alcohol, while we have found that our product dissolved after long-continued boiling with a large excess of alcohol.[2] In this, too, our results are at slight variance with Mulder's, so it may be that our product is not identical with Mulder's linoxyn, but it is more than likely that Mulder did not subject his linoxyn to as vigorous a solubility test as we have our product. Reference has already been made to our experiment regarding the solubility of our product (ether-insoluble) in chloroform and alcohol.

The oxidation product which separates from the ligroïn gives a larger amount of ether-soluble product if it is extracted at once than if the product is allowed to stand for some days before extraction. This may be due to a mechanical change in the oxidation product. When first separated, the product is less tenacious and more readily permeated by the solvent, than when it has, by exposure to the air, lost all of the adhering ligroïn by evaporation.

Noerdinger[3] has shown that linseed oil varnish will liberate iodine from potassium iodide and has ascribed this liberation to the presence of hydrogen peroxide. We have found that our oxidation product also, when in acetic acid solution, will liberate more iodine than is liberated from a blank test. The question arises whether or not this liberation of iodine from potassium iodide is due to hydrogen peroxide. This we must answer in the negative, for we have been unable to obtain any test for hydrogen peroxide, either with chromic acid or titanic acid. The liberation of the iodine is due to the presence of an organic peroxide.

In conclusion, it should be pointed out that the question of the solubility of the oxidation product (apart from its solubility in glacial acetic acid) was doubtless more or less affected by the presence of the lead and manganese of the drier.

[1] *Analyst*, **27**, 139 (1902).

[2] Except in the case of B_2 as has already been noted.

[3] *Pharm. Centrbl.*, **35**, 730 (1894).

[From the Laboratory of the Connecticut Agricultural Experiment Station.]

THE PRECIPITATION LIMITS WITH AMMONIUM SULPHATE OF SOME VEGETABLE PROTEINS.

By Thomas B. Osborne and Isaac F. Harris.

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Hofmeister and his students, who employed ammonium sulphate with much success in separating different proteins from one another, found that under suitable conditions the individual proteins are precipitated within quite narrow limits when this salt is added to their solutions up to certain degrees of saturation, which to a certain extent are characteristic for each protein. We have, therefore, applied this process to a number of the purer preparations of proteins which we had at our disposal.

A quantity of the protein was dissolved in one-tenth saturated ammonium sulphate solution, the solution filtered clear, and 2 cc. mixed with enough one-tenth saturated sulphate solution to make a final volume of 10 cc. with the saturated sulphate solution to be afterwards added. Successively greater quantities of the saturated solution were used and the points noted at which the solution first became permanently turbid, as well as that at which all the protein was precipitated, as shown by saturating the filtered solution with ammonium sulphate, and observing whether or not a precipitate or turbidity was produced. In many cases the filtrates contained minute quantities of something which was not precipitated with the bulk of the protein under examination, but could be afterwards precipitated from the filtrate by saturating with ammonium sulphate. In these cases we noted the point at which all but this trace was precipitated and also the point at which the solution finally became entirely clear. Whether this trace of substance, which is so much more difficult to precipitate than the bulk of the preparation, was a trace of contaminating proteose or some compound of the protein with some other substance or an alteration product produced by drying or in some other way during preparation, cannot now be told. However, in no case was more than an insignificant trace present and no serious contamination of the preparation is indicated by its presence. The "limits" here given are that at which the solution became turbid immediately after adding the saturated sulphate solution and that at which the protein

was first completely precipitated. Where a considerable further addition of sulphate was necessary to separate the final last trace, the point at which precipitation was practically complete is also given.

To determine the effect of concentration of the protein solution on the results of this determination, we tried the following experiments with neutral edestin.

Concentration of edestin solution. Per cent.	Lower limit. cc.	Upper limit. cc.
9.0	3.0	4.2
4.5	3.1	4.2
2.7	3.0	4.2

When 4.5 per cent. of edestin was dissolved in *10 per cent. sodium chloride,* the precipitation limits were lower, namely, 1.8 cc. and 3 cc. Edestin monochloride and edestin sulphate had essentially the same limits as the free edestin, although the lower limit for the sulphate was found to be a little below that of the others.

	Lower limit. cc.	Upper limit. cc.
2.37 per cent. of edestin monochloride.....	3.0	3.9
4.0 " " " " sulphate.....	2.5	4.2

The crystalline globulins of the squash-seed, flaxseed and castor bean are so nearly like that of the hemp-seed that until recently they have been regarded as the same protein. That this similarity extends to their relations toward ammonium sulphate is shown by the following figures:

	Protein. Per cent.	Lower limit. cc.	Upper limit. cc.
Edestin hemp-seed.....	2.7	3.0	4.2
Globulin flaxseed.....	3.4	3.1	4.7
Globulin squash-seed	3.6	3.3	4.4
Globulin castor bean.....	..	3.1	4.5

The globulin of the cottonseed, which we now recognize as another protein than edestin from the hemp-seed, has different precipitation limits from edestin, namely, for a solution containing 2.5 per cent. of globulin, a lower limit of 4.6 cc., and an upper one of 6.4 cc. In this we have another distinction between the cottonseed globulin and edestin. The globulin of the filbert (*Corylus tubulosa*) and that of the English walnut (*Juglans regia*) were

described by Osborne and Campbell[1] under the name of corylin, since a careful comparison of the reactions and analysis of a number of different preparations showed no difference between them. We have recently found[2] that the globulin of the filbert yields a little more ammonia, when decomposed with hydrochloric acid, than does the globulin of the English walnut, and we must therefore consider them to be distinctly different substances. This conclusion is supported by our determinations of the precipitation limits.

A solution containing 3.4 per cent. of the globulin from the filbert became turbid with 3.7 cc., was almost wholly precipitated with 5.3 cc., and completely with 6.6 cc. Under the same conditions a solution containing 2.75 per cent. of globulin from the English walnut became turbid with 2.8 cc., was almost wholly precipitated by 4.6 cc. and completely precipitated with 6.6 cc. That the last traces were precipitated, after nearly all of the globulin had been thrown out of solution, only by adding a considerably greater quantity of sulphate, indicates a slight contamination of the preparation with some other protein, possibly a trace of adhering proteose, possibly an alteration product of the globulin formed during drying or otherwise. However this may be, the amount was too small to be of serious consequence. The globulin of the American black walnut showed exactly the same behavior toward ammonium sulphate as that of the English walnut.

It is hence evident that the globulin of the English walnut is a different substance from that of the filbert and the name corylin should therefore be applied only to the latter.

Excelsin from the brazil nut and amandin from the almond have nearly the same precipitation limits although, otherwise, they are distinctly different substances. The lower limit for excelsin was found to be 3.8 cc., the upper 5.5 cc., while for amandin the lower limit was 3.5 cc. and the upper limit 5.3 cc. Preparations of legumin from different seeds, which have as yet appeared to be in all respects alike, showed the same precipitation limits with ammonium sulphate.

	Lower limit. cc.	Upper limit. cc.
1.8 per cent. legumin, vetch.....	5.2	7.3
3.2 per cent. legumin, horse bean.....	5.4	7.5
2.6 per cent. legumin, lentil.....	5.5	7.4

[1] This Journal, **18**, 609 (1896); also Report of the Conn. Agr. Expt. Station for 1895, p. 288.

[2] This Journal, **25**, 423 (1903).

Nearly all the legumin was precipitated in each case by 6.5 cc., that remaining in solution with more than this quantity being very little.

The globulin of the castor bean is partly precipitated from its concentrated solutions in 10 per cent. sodium chloride by saturating its solution with this salt. The precipitate thus produced, when redissolved in dilute brine, is again partly thrown out by saturating with sodium chloride, and as often as this process is repeated a considerable part of the globulin remains dissolved in the saturated salt solution. From this it seems more probable that the globulin has a limited solubility in saturated sodium chloride solution, which is much less than that in a 10 per cent. brine, than that two different globulins exist in the seed. The precipitation limits with ammonium sulphate also indicate that this is the case, as the following experiment shows. A quantity of this globulin, obtained by dialyzing a sodium chloride extract of castor beans, was dissolved in a moderate quantity of 10 per cent. brine, and the solution saturated with sodium chloride. The large precipitate was filtered out, again dissolved in brine, and the solution saturated with sodium chloride. The second precipitate appeared to be less than the first. The solution and precipitate were again repeated, when the final precipitate was dissolved in brine, and this solution, as well as the three filtrates from the precipitates produced by saturation, were dialyzed till free from sodium chloride. The substance separated from all four solutions as a mixture of crystals and spheroids, which were washed with water and dehydrated with absolute alcohol. After drying over sulphuric acid, the different preparations weighed as follows:

No. 1. 8.67 grams. This was the final precipitate produced by saturating with sodium chloride.

No. 2. 6.2 grams. The globulin remaining in solution after precipitating No. 1.

No. 3. 13 grams. The globulin remaining in solution after the second precipitation.

No. 4. 12.8 grams. The globulin remaining in solution after the first precipitation.

Since the substance yielding 1, 2 and 3 was precipitated by the first saturation with sodium chloride and two-thirds of this remained in solution after saturating the second and third time, it is

evident that precipitation is simply due to a limited solubility of this globulin in saturated salt solution. The smaller weight of No. 2 is due to the smaller volume of the solution from which it was obtained.

The precipitation limits of these preparations were as folows:

	Lower limit. cc.	Upper limit. cc.
No. 1	3.1	4.4
No. 3	3.16	4.5
No. 4	3.4	4.8

The slightly higher limits shown by No. 4 differ too little from those of the others to warrant the conclusion that two different proteins exist in these preparations.

The seeds of the yellow lupine contain a large amount of protein matter which can be separated into two extremes by fractional precipitation, which differ slightly from one another in properties and composition, especially in sulphur content, the more soluble fraction containing three times as much sulphur as the less soluble.

The precipitation limits were as follows:

	Lower limit. cc.	Most precipitated between. cc.	cc.	Upper limit. cc.
Conglutin (*a*) less soluble	4.2	4.3	6.0	*7.3
Conglutin (*b*) more soluble	4.6	6.4	8.2	8.7

From these results it is evident that the two extremes represent different proteins and that the more soluble one is precipitated at a much higher saturation than the less soluble one. It also appears that the separation of these two proteins from one another in the case of the preparations here tested, was not entirely complete.

The globulin from the blue lupine showed nearly the same behavior as the less soluble globulin of the yellow lupine, the lower limit being 4.4 cc., while with 6 cc. nearly all was precipitated.

Phaseolin is more soluble in strong solutions of ammonium sulphate than any protein we have yet examined. The lower limit was found with 6.4 cc. With 8.2 cc., which was all that could be added, under the conditions of the test as applied to the other globulins, there was still considerable protein in solution. When 1 cc. of the phaseolin solution was mixed with 9 cc. of the saturated solution all was precipitated. The upper limit appears to be, therefore, a little below 9 cc. The following table contains the

results of these determinations, arranged in the order of the solubility of each protein substance in ammonium sulphate solution.

Protein.	Lower limit. cc.	Most precipitated. cc.	Most precipitated. cc.	Upper limit. cc.
Globulin, English walnut	2.8	2.8	4.6	6.6
Globulin, black walnut	2.8	2.8	4.6	6.6
Edestin	3.0	3.0	4.0	4.2
Edestin monochloride	3.0	3.0	3.9	3.9
Globulin flaxseed	3.1	3.3	4.6	4.7
Globulin castor bean	3.1	3.3	4.3	4.5
Globulin squash-seed	3.3	3.5	4.1	4.4
Amandin	3.5	3.5	5.0	5.3
Corylin	3.7	3.7	5.3	6.6
Excelsin	3.8	4.0	5.0	5.5
Conglutin (*a*)	4.2	4.3	6.0	7.3
Conglutin (*b*)	4.6	6.4	8.2	8.7
Globulin cottonseed	4.6	5.0	6.0	6.4
Legumin	5.4	5.5	6.5	7.5
Phaseolin	6.4	6.5	8.2	8.8

[FROM THE LABORATORY OF THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION.]

THE SPECIFIC ROTATION OF SOME VEGETABLE PROTEINS.

BY THOMAS B. OSBORNE AND ISAAC F. HARRIS.

Received June 27, 1903.

THE specific rotation of very few of the vegetable proteins has been determined, the only observations, so far as we know, being those of Kjeldahl[1] on zein and gliadin, Alexander[2] on edestin, excelsin and the globulin of the flaxseed, and Chittenden and Mendel[3] on edestin. Having had an opportunity to make some observations on the proteins above named, as well as on a few others, we take this occasion to put then on record.

The determinations were made with a Schmidt and Haensch half-shade polariscope, provided with a sugar scale. The readings were calculated to degrees of circular polarization by multiplying the degrees observed on the sugar scale by 0.346. The results

[1] Kjeldahl: *Agricultur. Chem. Centrbl.*, **25**, 197 (1896).
[2] Alexander: *Jour. Expt. Med.*, **1**, No. 2 (1896).
[3] Chittenden and Mendel: *Jour. Physiol*, **17**, 40 (1894).

given were in all cases the average of a large number of observations, which in most cases agreed closely. The solutions of some of the proteins, although uncommonly clear and very nearly free from opalescence, were so opaque in long layers that satisfactory readings could be made only in comparatively dilute solutions and therefore the accuracy of these determinations was to a greater or less extent impaired.

The amount of dissolved protein was found by determining nitrogen in the contents of the polariscope tube, the capacity of which was accurately known. The amount of protein was obtained by multiplying the quantity of nitrogen found by a factor depending on the nitrogen content of the protein examined.

EDESTIN.

The preparation used had been repeatedly recrystallized and was perfectly neutral to phenolphthaleïn. A solution in 10 per cent. sodium chloride brine was filtered clear through a felt of paper pulp and examined with the following results:

I. α = observed rotation $-2.7°$.
w = weight of protein per cubic centimeter 0.03385 gr.
l = length of tube 2 dm.
$(\alpha)_D^{20°} = -40°$.

II. $\alpha = -2.07°$ $w = 0.0247$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -41.9°$.

III. $\alpha = -5.05°$ $w = 0.06095$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -41.43°$.

IV. $\alpha = -2.53°$ $w = 0.0610$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -41.47°$.

Another pure preparation of edestin gave the following results:

V. $\alpha = -1.73°$ $w = 0.0415$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -41.7°$.

The average of these results, —41.3°, agrees closely with that obtained by Alexander, namely,—41.6°, and does not differ greatly from that given by Chittenden and Mendel, —43°. There is no evidence that the degree of rotation is dependent on the concentration of the solution.

EXCELSIN.

The preparation of excelsin which we used was extracted from the brazil nut by sodium chloride brine and purified by recrystal-

lization. Although the solution in 10 per cent. sodium chloride brine used for polariscopic examination was almost free from every trace of opalescence, nevertheless, it was difficult to get satisfactory readings in strong solutions. Our results were as follows:

I. $\alpha = -3.38°$ $w = 0.0396$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -42.68°$.

II. $\alpha = -3.95°$ $w = 0.0463$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -42.66°$.

III. $\alpha = -2.00°$ $w = 0.0460$ gram $l = 1$ dm.
$-43.48°$.

The average of our figures, —42.94°, is considably higher than that of Alexander, —40.3°, but, as he appears to have been unable to get such clear solutions as we did and had great difficulty in making his readings, it is probable that our results are the more correct.

FLAXSEED GLOBULIN.

The carefully purified preparation of this globulin consisted of well-formed octahedral crystals, the solution of which, in 10 per cent. sodium chloride brine, when filtered, was so transparent that accurate readings were easily made.

I. $\alpha = -3.63°$ $w = 0.0415$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -43.73°$.

II. $\alpha = -1.79°$ $w = 0.0413$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -43.34°$.

The average of these determinations, —43.53°, is much higher than that found by Alexander, who gives —38.7° as the mean of six observations on different solutions. This difference may be due to the much greater concentration of our solutions, as Alexander's results strongly indicate a considerable decrease in the specific rotation with decreasing percentage content of the solution in protein.

SQUASH-SEED GLOBULIN.

The squash-seed globulin was purified by repeatedly recrystallizing and found to have the following rotation when dissolved in 10 per cent. sodium chloride solution:

I. $\alpha = -4.70°$ $w = 0.0598$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -39.3°$.

II. $\alpha = -4.12°$ $w = 0.0534$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -38.57°$.

III. $\alpha = -2.05°$ $w = 0.0535$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -38.32°$.

If we compare the average of these figures with those of the flaxseed globulin and of edestin, which were obtained with solutions of approximately the same strength, we find them as follows:

	$(\alpha)_D^{20°}$.
Edestin	41.30°
Flaxseed globulin	43.34°
Squash-seed globulin	38.73°

These three globulins appear therefore to differ in rotatory power to such a degree that the differences cannot be attributed to experimental errors. Although alike in composition, reactions, solubility and crystalline form, we have recently shown[1] that these globulins yield such different proportions of the several classes of nitrogenous decomposition products that there can be no question but that they are different substances. To these differences must now be added those in specific rotatory power.

AMANDIN.

Amandin, the chief protein constituent of almonds and peach-seeds, when dissolved in 10 per cent. sodium chloride solution, was found to have the following specific rotation:

$\alpha = -2.98°$ $w = 0.0264$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -56.44°$.

CORYLIN.

Corylin is a globulin which is abundantly present in the hazel nut or filbert. Dissolved in 10 per cent. sodium chloride solution it showed the following rotatory power:

I. $\alpha = -2.87°$ $w = 0.0332$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -43.22°$.

II. $\alpha = -1.40°$ $w = 0.0326$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -42.95°$.

[1] Osborne and Harris: This Journal, **25**, 323 (1903).

THE GLOBULIN OF THE ENGLISH WALNUT.

The English walnut contains a globulin which so closely resembles corylin in its properties and composition that the writer[1] was led to regard it as probably identical with that substance. We have since found that it yields, on decomposition, a slightly, but distinctly, smaller amount of ammonia than does corylin and that a difference between the two is shown by the precipitation limits with ammonium sulphate. In harmony with this, we find a slight difference in the specific rotation of their solutions in 10 per cent. sodium chloride brine, as the following figures show:

I. $\alpha = -1.57°$ $w = 0.0357$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -44°.$

II. $\alpha = -2.06°$ $w = 0.0227$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -45.37°.$

III. $\alpha = -1.05°$ $w = 0.0227$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -46.25°.$

The considerable differences between the above observations are chiefly due to the opacity of the solutions which, though filtered very clear, were, in a remarkable degree, impervious to light.

The specific rotation of the globulin of the English walnut is distinctly higher than that of the filbert, thereby showing another difference between these two very similar proteins.

THE GLOBULIN OF THE AMERICAN BLACK WALNUT.

The American black walnut is closely related to the English walnut and we have therefore made a close comparison of the globulins from these two nuts, but have discerned no notable difference between them. As the following figures show, the specific rotation of the globulin from American nut is practically the same as that of the one from English, the difference between the figures given being doubtless due to errors of observation caused by the opacity of the solutions. Dissolved in 10 per cent. sodium chloride solution, the following results were obtained:

I. $\alpha = -1.22°$ $w = 0.0272$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -44.85°.$

II. $\alpha = -1.20°$ $w = 0.0273$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -44.0°.$

[1] Osborne and Campbell: This Journal, **18**, 609.

PHASEOLIN.

Phaseolin, which constitutes the greater part of the protein matter of the kidney bean (*Phaseolus vulgaris*), was found to have the following rotation when a crystallized preparation was dissolved in 10 per cent. sodium chloride solution:

I. $\alpha = -7.42°$ $w = 0.0900$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -41.22°$.

II. $\alpha = -3.75$ $w = 0.0900$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -41.7°$.

LEGUMIN.

A solution of a very pure preparation of legumin from the horse bean (*vicia faba*) was made with 10 per cent. of sodium chloride and found to have the following specific rotation:

I. $\alpha = -2.2°$ $w = 0.0494$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -44.53°$.

II. $\alpha = -1.27°$ $w = 0.0291$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -43.64°$.

ZEIN.

The principal protein of maize kernels is zein, which is soluble in strong alcohol. A solution of zein in alcohol of 90 per cent. by volume rotated as follows:

I. $\alpha = -3.03°$ $w = 0.0536$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -28.26°$.

II. $\alpha = -1.45°$ $w = 0.0523$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -27.72°$.

GLIADIN.

Gliadin, which forms about one-half of the protein of wheat gluten, when dissolved in alcohol, of 80 per cent. by volume, showed the following specific rotation:

I. $\alpha = -5.66°$ $w = 0.0308$ gram $l = 2$ dm.
$(\alpha)_D^{20°} = -91.9°$.

II. $\alpha = -2.86°$ $w = 0.0309$ gram $l = 1$ dm.
$(\alpha)_D^{20°} = -92.55°$.

The following table contains the specific rotation as determined for each of the preceding proteins:

Protein.	Source.	$(\alpha)_D^{20°}$.
Edestin	Hemp-seed	−41.3°
Globulin	Flaxseed	−43.53°
Globulin	Squash-seed	−38.73°
Excelsin	Brazil nut	−42.94°
Amandin	Almonds	−56.44°
Corylin	Filbert	−43.09°
Globulin	English walnut	−45.21°
Globulin	Black walnut	−44.43°
Phaseolin	Kidney bean	−41.46°
Legumin	Horse bean	−44.09°
Zein	Maize	−28.00°
Gliadin	Wheat	−92.28°

[From the Laboratory of the Connecticut Agricultural Experiment Station.]

THE GLOBULIN OF THE ENGLISH WALNUT, THE AMERICAN BLACK WALNUT AND THE BUTTERNUT.

By Thomas B. Osborne and Isaac F. Harris.

Received June 27, 1903.

Proteins, whose chemical identity is probable, have thus far been found only in seeds which are botanically closely related to each other.

Thus the chemical identity of gliadin from wheat or rye, of legumin from vetches, horse beans, lentils or peas, of vicilin from the three latter seeds, of phaseolin from the kidney or adzuki beans and of legumelin from the seeds of numerous legumes appears to be highly probable.

The strict chemical identity of carbon compounds of such high molecular weight can, of course, not be positively asserted, since the possibility of isomeric or homologous compounds of very similar properties is great. However, a rigid comparison of these supposedly identical proteins has as yet shown no difference whatever between them. Some proteins, which we had formerly regarded as identical, have recently been found to differ in the proportions of their various decomposition products, and it is certain that their molecules have a different structure. All these proteins were found in seeds which were *not* botanically closely related and should therefore, by analogy, *not* contain the same proteins. So marked is this difference in the protein constituents

of the different seeds that the question may be asked: Is not this chemical difference in the food of the growing embryo an important factor in determining the nature of the developing organism?

Now that wide differences in the structure of the molecules of the different proteins are more fully recognized, it seems probable that the course of the chemical reactions, leading to the development of the growing embryo, will be largely influenced by the nature of the protein food presented to it at the beginning of its existence. Whether similar differences in the protein food of the animal embryo exists is not so definitely determined, but the few facts on record point strongly that way, for Panormoff's investigations indicate that hen's, dove's and crow's eggs contain distinctly different albumins.

The closest resemblance between proteins from unrelated seeds which we have as yet encountered is presented by corylin from the filbert (*corylus*) and the globulin from the English walnut (*Juglans regia*), the only difference, as yet discovered, being a slightly smaller yield of ammonia by the latter, when decomposed with hydrochloric acid, and a slight difference in the precipitation limits with ammonium sulphate.

In order to see if the same relations would be shown by the globulins from the botanically, closely related American black walnuts and butternuts (*Juglans nigra* and *J. cinera*) we have examined these nuts with the following results.

THE GLOBULIN OF THE BLACK WALNUT (*Juglans nigra*).

The nuts were freed from their shells, crushed, the greater part of the oil pressed out and the remainder extracted with ether. The residual meal was then extracted with 10 per cent. sodium chloride solution, the extract filtered clear and dialyzed. The globulin was deposited in spheroids which were filtered out, washed thoroughly with water and then with alcohol, and dried over sulphuric acid. Dried at 110°, this preparation had the following composition:

BLACK WALNUT GLOBULIN, PREPARATION I.

Carbon	50.95
Hydrogen	7.10
Nitrogen	18.84
Sulphur	0.78
Oxygen	22.33
	100.00
Ash	0.38

This preparation was then dissolved in 10 per cent. sodium chloride solution, a large quantity of the insoluble form of the globulin filtered out and the clear solution dialyzed for several days. The globulin, which again precipitated in spheroids, was filtered out, washed with water and with alcohol and dried over sulphuric acid. The 32 grams thus secured, which formed about one-half of the original material, had, as the following figures show, essentially the same composition, when dried at 110°, as the preparation from which it was derived.

BLACK WALNUT GLOBULIN, PREPARATION 2.

	I.	II.
Carbon	51.06	51.07
Hydrogen	6.87	6.84
Nitrogen	18.96	18.96
Sulphur	0.77	....
Oxygen	22.34	....
	100.00	
Ash	0.33	

This preparation was almost wholly soluble in 10 per cent. sodium chloride solution and showed the same reactions as those given in an earlier paper for the globulin of the English walnut.[1] A solution containing about 5 per cent. of the globulin and 10 per cent. of the sodium chloride remained clear until heated to 99°, when it became turbid and, after continued heating, yielded a considerable coagulum. Solutions of the globulin from the English walnut yielded a trace of coagulum at lower temperatures, which was unquestionably due to a trace of another protein, adhering to the preparation in minute quantity. Saturation of the solution with sodium chloride gave a very slight precipitate and with magnesium sulphate a very considerable one, in this respect exactly resembling the globulin of the English walnut. The other reactions were also, in all respects, the same.

When decomposed by boiling with strong hydrochloric acid, the proportion of nitrogen in the different forms of binding were as follows:

N as NH_3.	Basic N.	Non-basic N.	N in MgO precipitate.	Total.
1.71	5.61	11.45	0.19	18.96
1.86	5.85	10.92	0.33	....
1.83	5.85	11.04	0.24	....

The specific rotation of this globulin was determined as follows:

[1] This Journal, **18**, 609 (1896).

Solvent.	Amount per cc. Gram.	Observed rotation.	Length of tube.	Specific rotation. $(\alpha)_D^{20°} =$
10 % NaCl	0.0272	1.22°	1 dm.	−44.85°
.....	0.0273	1.20°	1 dm.	−44.0°

The precipitation limits with ammonium sulphate were determined by making a 2.7 per cent. solution of the globulin in one-tenth saturated ammonium sulphate solution and then adding different quantities of a saturated solution of ammonium sulphate to 2 cc. of the globulin solution previously diluted with enough one-tenth saturated to make a final volume of 10 cc.

The mixture became turbid when the amount of sulphate was equal to that in 2.8 cc. of a saturated solution. When sulphate equal to 4.6 cc. was added, only a very minute quantity of protein remained unprecipitated, which was doubtless a trace of some other adherent protein. With less than 4.6 cc. the amount in solution was greater. The precipitation limits are therefore 2.8 cc. and 4.6 cc.

THE GLOBULIN OF BUTTER NUT (*Juglans cinerea*).

The preparation of this globulin, which we examined, was very kindly given to us by Dr. A. L. Dean, of Yale University, for which we here wish to express our thanks. Dr. Dean extracted the crushed meats of the nut with petroleum ether and exhausted the residual meal with 10 per cent. sodium chloride solution. The clear, filtered extract was dialyzed in running water for seven days when the globulin, which separated in spheroids, was filtered out and washed witn water, with alcohol and with ether. As the quantity of the globulin was not sufficient for further purification by reprecipitation, it was examined in the condition in which it was received.

Dried at 110° it had the following composition:

Butter-nut Globulin, Preparation 1.		
Carbon	50.85	50.91
Hydrogen.....	6.79	6.88
Nitrogen.....	18.62	18.59
Sulphur	0.80	....
Oxygen	22.94	....
	100.00	
Ash.....	3.54	3.67

This preparation was almost completely soluble in 10 per cent. sodium chloride solution and showed throughout the same reactions as those given by the globulins of the English and black walnut.

When decomposed by boiling with strong hydrochloric acid, the proportion of nitrogen in the different groups of nitrogenous decomposition products was as follows:

N as NH_3.	Basic N.	Non-basic N.	N in MgO precipitate.	Total.
1.83	5.77	10.87	0.14	18.61

The specific rotation of this globulin was found as follows:

Solvent.	Amount per cc.	Observed rotation.	Length of tube.	Specific rotation. $(\alpha)_D^{20°} =$
10 % NaCl	0.0212	1.97°	2 dm.	−46.9°
10 % NaCl	0.0223	0.98°	1 dm.	−43.9°

The precipitation limits of a 4 per cent. solution of the globulin, dissolved in one-tenth saturated ammonium sulphate, were determined in the same manner as for the black walnut globulin and found to be 3.1 cc. and 5.5 cc., the amount remaining in solution with 5.5 cc. being more than in the case of the black walnut, at the higher limit, which was doubtless due to the lack of sufficient purification of this preparation, and possibly also to a difference in acidity between the preparations examined.

SUMMARY.

In the following table the results of our examination of the globulin from the seeds of the three species of *Juglans* are brought together for comparison with those of the globulin of the filbert, *Corylus*.

COMPOSITION.

	J. regia.	*J. nigra.*	*J. cinerea.*	*Corylus.*
Carbon	50.80	51.07	50.88	50.72
Hydrogen	6.84	6.86	6.84	6.86
Nitrogen	18.96	18.96	18.62	19.02
Sulphur	0.80	0.77	0.80	0.83
Oxygen	22.51	22.33	22.86	22.57
	100.00	100.00	100.00	100.00

PERCENTAGE OF NITROGEN IN THE GROUPS OF NITROGENOUS DECOMPOSITION PRODUCTS.

	N as NH_3.	Basic N.	Non-basic N.	N in MgO precipitate.
J. regia	1.84	6.08	10.93	0.11
J. nigra	1.80	5.77	11.14	0.25
J. cinerea	1.83	5.77	10.87	0.14
Corylus	2.20	5.75	10.70	0.16

SPECIFIC ROTATION $(\alpha)_D^{20°}$.

J. regia	−45.21°
J. nigra	−44.42°
J. cinerea	−45.40°
Corylus	−43.09°

PRECIPITATION LIMITS WITH AMMONIUM SULPHATE.

J. regia	2.8 cc.	−4.6 cc.
J. nigra	2.8 cc.	−4.6 cc.
J. cinerea	3.1 cc.	−5.5 cc.
Corylus	3.7 cc.	−5.3 cc.

The only positive difference shown by the preparations from these four seeds is the greater quantity of N yielded as ammonia by the globulin from the filbert (*Corylus*). This difference exceeds the limits of experimental error by too great an amount to be overlooked and may be taken as evidence that the globulin of *Corylus* differs in structure from that of *Juglans.* A positive difference between the corylin and the globulin from *J. regia* and *J. nigra* is also shown by the precipitation limits with ammonium sulphate. This difference, however, is not very great and, in view of our ignorance of the extent to which these limits may be altered by slight differences in the conditions of experimentation, cannot be considered as conclusive evidence, though it strongly indicates a difference between the globulins.

The precipitation limits of the globulin from *J. cinerea* are higher than those found for *J. regia* and *J. nigra,* but in view of the very close agreement between these preparations in all other respects we are inclined to attribute this difference to the greater purity of the preparations from the latter seeds.

In consequence of these facts, it seems desirable to give a name to the globulin of Juglans, retaining the designation corylin for the globulin of *corylus.* We propose therefore to call the principal protein which we have obtained from the nuts of the three species of the former genus Juglansin.

The botanical relations which are shown by the proteins of seeds deserve further careful study, as it is not improbable that the natural relations of some plants may be thus discovered.

[From the Laboratory of the Connecticut Agricultural Experiment Station.]

THE TRYPTOPHANE REACTION OF VARIOUS PROTEINS.

By Thomas B. Osborne and Isaac F. Harris.

Received June 27, 1903.

As long ago as 1831, Tiedemann and Gmelin recognized among the decomposition products of protein bodies a substance whose solution was colored a deep violet-red with chlorine or bromine. The nature of this substance remained wholly unknown until Hopkins and Cole recently succeeded in isolating it in a state of purity and recognizing it as most probably indol-amino-propionic

acid or the isomeric skatol-amino-acetic acid. They also found that this substance yielded the violet reaction with acetic and sulphuric acid, which has long been known as Adamkiewic's reaction. This latter reaction they further found was caused by glyoxylic acid contained in the acetic acid, and they have therefore substituted glyoxylic acid for acetic acid in applying this test. This observation is of much importance, as formerly the Adamkiewic reaction was attributed to furfural and the presence of carbohydrates was therefore inferred among the protein decomposition products.

In the following table we give the results of the application of the Hopkins-Cole reagent to a number of different proteins, 50 mg. of each being mixed with 6 cc. of the glyoxylic acid solution and 6 cc. of concentrated sulphuric acid added.

Zein, maize ; very pale straw color ; no reaction.	
Alcohol-soluble protein, oat kernel ; light brownish ; no violet tint.	
Bynin, malt ; red-brown ; no violet tint whatever.	
Vicilin, pea ; very pale violet ; hardly any reaction.	
Phaseolin, kidney bean ; pale violet ; a little stronger than vicilin.	
Avenalin, oat kernel ; light violet color.	
Globulin, wheat ; light violet color.	
Hordein, barley ;	The intensity of the reaction increased gradually from hordein to leucosin, the former giving a positive reaction, the latter a strong one.
Legumin, vetch ;	
Legumin, lentil ;	
Legumin, horse bean ;	
Vignin, cow pea ;	
Conglutin, yellow lupine ;	
Conglutin, blue lupine ;	
Amandin, almond ;	
Glycinin, soy bean ;	
Gliadin, wheat ;	
Ovovitellin, hen's egg ;	
Globulin, sunflower ;	
Glutenin, wheat ;	
Globulin, castor bean ;	
Edestin, hemp ;	
Excelsin, Brazil nut ;	
Corylin, filbert ;	
Conalbumin, egg white ;	
Ovalbumin, egg white ;	
Globulin, flaxseed ;	
Globulin, squash-seed ;	
Globulin, black walnut ;	
Globulin, English walnut ;	
Leucosin, wheat ;	

Whether any of the above proteins wholly lack the tryptophane group could not be determined, as we were able to get a very slight reaction with a relatively large quantity of zein by cautiously adding the sulphuric acid up to one-half the volume of the glyoxylic acid. The color thus produced was, at the most, very slight and transitory. With the alcohol-soluble proteins of the oat and barley malt, the brown color was sufficient to obscure a slight violet reaction, and the result of the test in these cases was not conclusive.

It is interesting to note the very marked difference in the intensity of the reaction with the proteins at the two ends of the table and it is fair to presume that the proportion of tryptophane yielded by the several proteins differs considerably.

[CONTRIBUTIONS FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE, NO. 49.]

DISAPPEARANCE OF REDUCING SUGAR IN SUGAR-CANE.

BY H. W. WILEY.

Received June 11, 1903.

THE occurrence of reducing sugar in sugar canes and sorghums has important relations to the metabolism of the plants. Presumably the carbohydrate which is finally formed in the chlorophyl cells of these plants is some variety of starch, probably a soluble variety, since starch granules, as such, would find obstructions to circulation in the return currents from the leaves to the body of the plant. During the early stages of growth it has been shown by repeated analyses that the proportion of reducing sugar to sucrose in the juices of the sugar cane is very high. In Louisiana, where the canes are harvested necessarily before growth is complete, the average quantity of reducing sugars in the juice is 1 per cent. or more. In the tropics at the time of harvest the percentage of reducing sugars is very much less, usually less than 0.5 per cent. These facts show beyond doubt that the highest relative value of reducing sugar to sucrose is in the earlier stages of growth and the lowest proportion in the matured stages. Theoretically, then, we might expect that at a certain period representing the complete and perfect maturity of the plant the reducing sugar would disappear. The further

phenomenon, however, has also been observed, namely, that when the reducing sugar has been reduced to a minimum on approaching maturity, any deterioration in the plant, due to long standing, overripeness, injury (from frosts or otherwise), tends to reverse the order observed during the growing period, and to increase the percentage of the reducing sugar at the expense of the sucrose. This reversibility of enzymic action has been well established in the case of carbohydrates.[1] If the sugar cane, therefore, be allowed to normally grow and mature, there is a certain time in its history, as above mentioned, where the proportion of reducing sugar is at a minimum. The theory above outlined receives confirmation in some analytical data secured in this bureau recently on samples of sugar cane grown in Florida. Four samples were obtained which were all harvested at the same time, namely, the middle of May, 1903. The canes were grown by W. H. Abel, on Terra Ceia Island, Manatee County, Florida, about 150 yards from salt water. The soil is sandy to a depth of from 12 to 18 inches, with a thin stratum of chocolate-colored subsoil resting on clay, which carries some pebble phosphate. The particular samples under question were grown on the edge of a field next to timber, and being in the outside row, did not get much cultivation and practically no fertilizer. The samples were cut seventeen months from time of planting. The analytical data obtained from the four samples are as follows:

COMPOSITION OF THE JUICE.

Density. Per cent.	Sucrose. Per cent.	Purity.	Glucose.
21.0	19.0	90.5	None
20.8	18.7	90.0	None
20.4	18.0	88.2	None
21.7	19.8	91.2	None

These are the only samples of sugar cane ever analyzed under my supervision which did not contain a greater or less quantity of reducing sugar. At the end of two minutes' boiling of the juices with an alkaline copper solution, there was no trace whatever of any reduction. On longer continued boiling and after allowing to stand over night, there was a mere trace of reddish precipitate, due doubtless to the inversion of a part of the sucrose. A great many of the canes grown on this field produced tassels, but Mr. Abel did not state in his description whether the four canes sent had

[1] *Jour. Chem. Soc. Trans.*, May, 1903, p. 578.

tasseled or not. The presumption is that they had. We have in the above what appears to be an example of a complete cycle of growth in the sugar cane, probably a cycle which would not be realized farther south. Evidently the cool nights of the winter had helped to complete the period of growth, while at the same time they prevented a beginning of the second growth, which would certainly have reversed the metabolic activities within the cane and secured an inversion of a part of the sucrose. It is probable that the meteorological conditions which produced so complete a growth do not often obtain and the above data are therefore of interest, both from a chemical and physiological point of view. The analyses were made in the Sugar Laboratory by Mr. Arthur Given.

COLORING-MATTER IN YELLOWISH GRAY SUGAR.

By Y. Nikaido.

Received June 27, 1903.

The crystallized sugar we obtained from the last few straight pans in the 1902 campaign, at the sugar factory operated by the Standard Beet Sugar Co., Leavitt, Neb., acquired a slight yellowish gray tint. The samples were saved and subjected to investigation. Since we could not make a series of investigations at this time of the year, the work is not complete, but some of the statements may be interesting to sugar-makers.

Herzfeld considers iron oxide as one of the causes of the gray coloration of crystallized sugar.[1] For this reason, the sample of sugar in question was tested qualitatively. Iron oxide, lime, soda and potash salts and a little organic coloring-matter were found in it. In order to ascertain how much iron oxide in the massecuite is sufficient to produce a yellowish tint in the sugar crystals, the quantity of the iron oxide in the massecuite sample was estimated and found to be 0.02 per cent. As it seemed doubtful that such a small amount of iron oxide in the massecuite would cause the coloration of sugar crystals, complete analyses of the massecuite and ash of the same were made and the results obtained were as follows:

[1] *Ztschr. Rubenzuckerind.*, **46**, 1 (1896).

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[1] *Ztschr. Rubenzuckerind.*, **46**, 1 (1896).

MASSECUITE.

Constituents.	Per cent. in water-free material.
Sucrose	84.76
Invert sugar	0.93
Raffinose	2.38
Ash	3.34
Organic matter	8.57
Iron oxide	0.02
	100.00

COËFFICIENTS CALCULATED.

	Per cent.
Total solid	89.83
Water	10.17
Polariscope reading	79.90
True purity	84.76
Saline coëfficient	25.38
Glucose coëfficient	1.10
Coëfficient of organic matter	9.89

ASH.

	Per cent.
Acid-insoluble matter (mostly silica)	0.80
Iron oxide (Fe_2O_3)	0.65
Calcium carbonate	13.86
Sodium chloride	7.06
Sodium carbonate	16.99
Potassium sulphate	28.94
Potassium carbonate	29.80
Magnesia	trace
Moisture and undetermined	1.90
	100.00

According to these analyses, excepting raffinose, there is no unusual constituent in this massecuite, judging from the analysis of another massecuite which yielded a good quality of white sugar. For the purpose of comparison, a statement of this analysis is here given:

Composition.	Per cent. in water-free material.
Sucrose	83.83
Invert sugar	3.34
Raffinose	none
Ash	4.88
Organic matter	7.95
Iron oxide, less than	0.01
	100.00

COËFFICIENTS CALCULATED.

	Per cent.
Total solid	90.50
Water	9.50
Polariscope reading	79.00
True purity	83.83
Saline coëfficient	17.17
Glucose coëfficient	3.98
Coëfficient of organic matter	9.48

Raffinose in considerable quantity is said to have the effect of changing the normal form of sugar crystals, producing needles, but it has nothing to do with the coloring of the sugar. It may, therefore, safely be said that the coloring of our sugar was principally due to the iron oxide, although the other impurities might have played some part. It would be worth noting that even such a small quantity of iron oxide as 0.02 per cent. is sufficient to cause coloration of sugar crystals.

In order to trace the source of the iron oxide, the limestone used for defecation was analyzed. It seemed possible that the rock might have contained an unusually large quantity of iron oxide. Since *oxide of iron is soluble in sugar solution even in the presence of alkali,* it was reasonable to suppose that iron might have been thus introduced in the carbonation process. The results of the limestone analysis are as follows:

	Per cent.
Moisture	trace
Insoluble matter	1.96
Organic matter	trace
Alumina (Al_2O_3)	0.33
Iron oxide (Fe_2O_3)	0.47
Calcium carbonate	96.53
Magnesium carbonate	0.38
Phosphoric acid	trace
Soda and potash	trace
Sulphuric acid	trace
	99.67

The above figures computed to a basis of burned lime give the following:

	Per cent.
Insoluble matter	3.41
Alumina (Al_2O_3)	0.57
Iron oxide (Fe_2O_3)	0.82
Calcium oxide	94.53
Magnesium carbonate	0.66
	99.99

It may be seen that this lime contains very little iron oxide. It is evident therefore that we must look elsewhere for the sources of the iron which caused the trouble in the pan.

Some iron doubtless came from the lime, and some unquestionably came from the water used in diffusion. The water from the Leavitt well was found to contain 0.0024 per cent., or 24 parts per 100,000 of oxide of iron.

Quite recently a sample of lime removed from the kiln by Superintendent H. Schmode was subjected to analysis and found to be radically different in composition from the first sample analyzed. The results of this analysis are here given:

	Per cent.
Acid-insoluble matter	26.10
Acid-soluble silica	0.26
Lime (CaO)	63.44
Magnesia (MgO)	0.11
Alumina (Al_2O_3)	3.97
Iron oxide (Fe_2O_3)	2.09
Carbon dioxide (CO_2)	3.05
Sulphuric acid (SO_3)	0.14
Undetermined	0.84
	100.00

There is certainly sufficient iron oxide shown in this sample to have caused all the disturbances noted. These two analyses would indicate a decided lack of uniformity of composition in the lime rock used at the factory.

To sum up the whole matter, it is my opinion that the coloring of the sugar in the massecuite was due to iron oxide. The source of this iron is still an open question, but the evidence at hand points rather clearly to the lime rock as the origin of it.

The author wishes to express his gratitude to Prof. H. H. Nicholson, as the investigation has been carried on in the chemical laboratory of the University of Nebraska by his permission.

SOME CHEMICAL CONSTANTS OF FOSSIL RESINS.[1]

By R. A. Worstall.

Received June 24, 1903.

While the literature relating to the resins in general is quite extensive, it is nevertheless true that published data, in regard to

[1] Read before the International Congress of Applied Chemistry at Berlin, June, 1903.

the chemical constants of those fossil and semi-fossil resins which enter into the composition of varnishes, are quite scarce. Several investigators[1] have published results obtained from specimens of a few of these resins, but their results are in general of little or no value for various reasons. In the first place, many authors have not taken pains to properly classify the particular resins with which they were working. Then, too, their work has in many cases been with single specimens and not sufficient data are available for any one resin from which definite conclusions may be drawn. Last, but not least, as K. Dieterich has pointed out in his excellent book upon the analysis of resins,[2] the methods employed for resins in general have not been either accurate or uniform. Almost without exception the methods for the analysis of fats have been applied to the resins—a class of compounds entirely different from the fats in origin and constitution, so that we have ester values of resins which contain no esters, direct acid numbers which are far too low, and a general lack of concordance in the results.

It is chiefly due to Tschirch and his pupils that we have a clearer idea as to the origin and chemical constitution of the resins, while to K. Dieterich we owe quite as much from the analytical point of view. The later, in the book previously referred to, has given us suitable methods of analysis for each resin, and applied these methods in determining the constants of many species. The work herein recorded was undertaken to extend our information concerning the fossil and semi-fossil resins—the so-called "Copals"—a subject to which Dieterich has given but brief attention,—with the hope of developing a rational scheme of analysis. Each specimen was taken from large shipments, and represents a fair average sample of a definite commercial grade. As many different specimens as it was possible to secure were examined, in the belief that from a large number of data better conclusions could be drawn. As descriptions of the physical properties and characteristics of these various resins are to be found in several books treating of such subjects, it has seemed best to omit all such data from consideration in this article, giving for each resin no more description than is necessary to properly classify it.

KAURI COPAL.

Kauri resin, or Kauri copal, a semi-fossil, was originally an

[1] For a complete bibliography of this subject see "Die Harze und die Harzebehälter," by Tschirch.

[2] "Analyse der Harze, Balsame, und Gummiharze."

exudation from the pine tree of New Zealand—*Dammara Australis*—and is found only in the province of Auckland in open bush land from which the original forests have disappeared. In other parts of the colony, forests of these trees still exist which yield, on tapping, a soft spongy sap, while an intermediate quality of a semi-matured state—"bush Kauri"—also exists, which time might convert into semi-fossil variety. The data herein given refer entirely to the semi-fossil resin. The quantity of Kauri consumed annually in the United States more than equals that of all the other fossil and semi-fossil resins combined.

ACID NUMBERS.

In determining the acid numbers of Kauri the indirect method of Dieterich was followed, with a modification in the solvents used. One gram of the finely powdered resin was weighed out into a glass-stoppered bottle, and 15 cc. benzene and 5 cc. alcohol were added. Solution is complete in a few minutes with these solvents. Then 15 cc. of fifth-normal alcoholic potash were run in, the bottle tightly stoppered and allowed to stand eighteen hours, 25 cc. of alcohol then added and the excess of alkali titrated back with fifth-normal sulphuric acid, using phenolphthaleïn as an indicator. The method gives sharp end-reactions and closely agreeing duplicates. Blank determinations were run each time, using the same quantities of solvents.

As Dieterich has pointed out, direct titration gives acid values far too low for all resins, because the complete neutralization of the resin acids proceeds slowly. To illustrate this point the following experiment will serve. Several portions of a sample of Kauri, whose acid number had been accurately determined as 103, were weighed out and the acid number determined by indirect titration at different intervals of time. The results were as follows:

Time.	Acid number.
5 minutes	82
1 hour	92
3 hours	96
6 "	101
12 "	102
18 "	103

It is very necessary, as Dieterich has also observed, that rather strong acid be employed for the titration, as the addition of much

water hydrolyzes the potassium salts and lowers the apparent acid number. The author has found the addition of alcohol before the titration a great help in securing sharp end-reactions.

At the very beginning of this work it became evident that there was a wide divergence between the acid values of different samples of Kauri, ranging from a minimum of 72 to a maximum of 142, the large lumps ("bold" gum) having always the lowest acid values, the fine chips and dust the highest. Dieterich, who had noted with other resins, especially dammar, that the dust had much higher acid numbers than the large lumps, at once concluded that this must be due to adulteration of the dust with colophony. But as all the resins herein described were taken from original packages which had not been opened since leaving Auckland, the author was convinced that no adulteration was possible.

Dieterich has condemned the iodine and bromine numbers as of no value when applied to resins, and has omitted those determinations in his schemes of analysis. That he is entirely mistaken—at least in so far as the Copals are concerned—will appear from the following results. Proof that these Kauri samples were not adulterated was afforded at once when the iodine values were determined. The latter ranged from a maximum of 170 to a minimum of 74, the iodine value being always at a *maximum* when the acid number was at a *minimum,* and decreasing directly as the acid number increased. As colophony has an acid number of 160 and an iodine value of 170, adulteration with the latter would have caused a simultaneous increase in both acid and iodine values.

In determining the iodine value, the usual Hübl method was employed, using a large excess of iodine solution, and allowing to stand eighteen hours before titrating.

The following table shows the results obtained from forty-three specimens of Kauri resin.

Number.	Description.	Acid.	Iodine.
1	XXXX White, large lumps	72	170
2	XX Brown, " "	72	154
3	X White, " "	72	162
4	Brown one, " "	77	140
5	X Brown, " "	77	160
6	X Nubs, white, large	76	154
7	XX " " "	76	159
8	No. 1 " " "	85	146

Number.	Description.	Acid.	Iodine.
9	X Nubs, brown, large	87	148
10	No. 1 " white, "	87	144
11	No. 1 " " "	87	149
12	No. 1 " " "	91	142
13	Chips, white, large	80	153
14	" " "	82	159
15	" " "	79	151
16	" brown "	86	162
17	" light, medium	96	143
18	" " "	99	143
19	" " "	92	137
20	" " "	97	140
21	" " "	95	137
22	" brown, "	89	132
23	" light, small	112	115
24	" dark, "	113	110
25	" and dust	111	115
26	Small brown chips	92	124
27	Bright fine chips	103	120
28	" " "	103	125
29	" " "	107	113
30	" seeds	107	113
31	Medium "	103	113
32	" "	108	111
33	" "	122	105
34	" "	123	105
35	" "	122	107
36	Dark "	125	95
37	Bright dust	118	105
38	" "	120	105
39	Medium "	127	93
40	" "	130	87
41	" "	123	82
42	Brown "	133	89
43	" "	142	74

While no particular relation could be expected to exist between two arbitrary values such as the acid numbers and the iodine absorption, it is worth noting that the sum of these two values is approximately a constant. For the forty-three specimens the average of this sum is 228, the maximum being 248 and the minimum 205. And if for each specimen the percentage of impurities is taken into consideration and these values estimated for the pure resin contained, the divergence is less marked. In other words, the iodine number decreases in almost exact proportion as the acid number increases, and *vice versa*.

From the researches of Tschirch and his pupils, it appears that the copals consist of "resenes"—neutral compounds containing oxygen and possibly of aldehyde nature— and of the resin acids. Other investigators[1] have noted the fact that the copals will absorb oxygen, and evidently the increase in acid number and decrease in iodine absorption is due to oxidation of these "resenes," by contact with the air, to resin acids, and that heretofore the finer the particles of the resin and the more porous they are, the higher will be their acid number. That this increase in the acid number is actually due to oxidation, the following experiments will illustrate.

A number of samples of Kauri were selected, each one finely powdered, and its acid and iodine numbers determined. These samples were then left four months in open bottles exposed to the air, and the powdered resins stirred from time to time to promote oxidation. At the end of this time their constants were again determined with the following results:

	Before oxidation.		After oxidation.			
Number.	Acid.	Iodine.	Acid.	Iodine.	Acid. Increase.	Iodine. Decrease.
1	72	154	87	133	15	21
2	76	159	111	121	35	38
3	77	140	93	115	16	25
4	72	170	107	110	35	60
5	97	109	104	99	7	10
6	105	113	109	112	4	1

Samples 1, 2, 3 and 4 were hard, "bold" gum of highest quality, while samples 5 and 6 were of a soft, spongy, lowest grade Kauri, in which oxidation had already made much progress before the experiment was carried out.

This oxidation proceeds rapidly in presence of alkalies, so that open saponification with alcoholic caustic potash gives acid numbers that are much too high. Doubtless this fact, in connection with the impossibility of obtaining correct acid numbers by direct titration, has led to the reporting of ester values in resins where no esters exist. That Kauri is free from esters was shown by saponifying several samples in flasks with return condensers, digesting for one hour on the steam-bath. In every case the saponification number thus found was the same as the indirect acid number.

[1] See Kiessling, Weger, and Lippert: *Chem. Rev.*, **98**, I, 286; *Ztschr. angew. Chem.*, **98**, I, 1248.

MANILA COPAL.

This semi-fossil resin comes from the islands in the Malay Archipelago. Its botanical source is unknown. Commercially it is second to Kauri in the amount consumed each year in the United States for varnishes. Nineteen samples were taken from direct importations, the acid and the iodine values being determined by the same methods employed for Kauri, with the following results:

Number.	Description.	Acid.	Iodine.	Sum of acid and iodine.
1.....	Finest white, "bold"	146	148	294
2.....	Medium " "	167	128	295
3.....	" " "	175	132	307
4.....	Hard brown "bold"	176	131	307
5.....	White Nubs	165	135	300
6.....	Medium white Nubs	176	125	301
7.....	Amber Nubs	180	125	305
8.....	White chips	176	127	303
9.....	" "	178	131	309
10.....	Medium chips	180	129	309
11.....	" "	180	125	305
12.....	Amber chips	182	119	301
13.....	" "	182	117	299
14.....	" "	186	119	305
15.....	" "	187	120	307
16.....	" "	187	116	303
17.....	" "	188	119	307
18.....	" "	190	120	310
19.....	Dust	199	104	303

It will be noticed that the sum of the acid and the iodine values is in each case quite near the average, 304, and that the less marked increase in acid values as the size of the gum decreases indicates that oxidation by the air is not so rapid as in the case of Kauri. The effect of oxidation was determined just as for Kauri by allowing the finely powdered resin to stand in contact with the air for four months. The following table shows the results:

		Before oxidation.		After oxidation.	
Number.	Description.	Acid.	Iodine.	Acid.	Iodine.
1.....	Hard brown, "bold"	176	131	183	128
2.....	" white, "	142	148	146	144
3.....	White chips	186	119	189	113
4.....	Medium chips	180	125	191	112
5.....	" white, "bold"	175	132	178	122
6.....	" " "	167	133	178	128

Oxidation, therefore, does not proceed as rapidly or as far with Manila as with Kauri. Open saponification, however, gives too high results. Closed saponification gives the same figures as the indirect acid numbers, showing the absence of esters.

PONTIANAC COPAL.

One of the most recently exploited copals is the so-called "Pontianac," a semi-fossil from the Malay archipelago. In many ways it seems to be a connecting link between Kauri and Manila, not only in its physical characteristics, but also in its chemical constants. At present the consumption of the resin in the United States is in an experimental stage, and only two samples were available.

		Before oxidation.		After oxidation.	
Number.	Description.	Acid.	Iodine.	Acid.	Iodine.
1	Medium chips	135	142	153	104
2	Small "	143	119	157	102

It will be noted that its acid and iodine values lie between those of Kauri and Manila, and that it is more easily oxidized than Manila, but not so readily as Kauri. In its physical properties it more closely resembles Manila. It contains no esters.

SOUTH AFRICAN FOSSIL COPALS.

Zanzibar, Madagascar and Mozambique copals, the hardest and probably the most ancient of the fossil copals, are all found on the southeast coast of Africa. The botanical source of Zanzibar copal is probably the trachylobium verrucosum, and it is probable that the other two varieties of resin come from closely related species. Zanzibar is still of commercial importance, but Madagascar and Mozambique are but little used in the United States.

The acid numbers, iodine absorptions, and effect of oxidation were determined for these resins just as for those previously described.

		Before oxidation.		After oxidation.	
Resin.	Description.	Acid.	Iodine.	Acid.	Iodine.
Zanzibar	Prime white "sorts"	79	123	79	123
"	Amber chips	104	115	102	114
Mozambique	White "sorts"	80	136	107	108
Madagascar	Amber "sorts"	95	126	100	106

Zanzibar does not seem to be readily oxidized. None of these resins contained esters.

WEST AFRICAN FOSSIL COPALS.

Of the west African copals, the following were examined: "North Coast" or "Akra," red and white Angola, Congo and Benguela. The botanical source of these resins is not known positively. The following table gives the results:

Resin.	Description.	Before oxidation.		After oxidation.	
		Acid.	Iodine.	Acid.	Iodide.
North Coast	White, "bold"	108	143	127	109
" "	" "	109	143	125	122
" "	" "	116	140	137	116
Benguela	" "	139	142	161	121
Congo	" "	150	122	150	116
"	No. 2 "	152	122	153	109
Red Angola, select		143	130	142	115
White " "		127	136	128	118

It may be remarked that the effect of oxidation upon all resin described in this paper was studied in the same manner as for Kauri, by leaving the finely powdered resin in contact with the air for four months. It is worth noting that while oxidation does not increase the acid numbers of Congo or the Angolas, it materially decreases the iodine absorption. The reason for this is not clear. None of these copals contain esters.

SIERRA LEONE COPAL.

Sierra Leone copal is the exudation from the bark of the *Copaifera Guibourtiana,* on the west coast of Africa. This tree flourishes in the elevated mountainous districts. The gum is gathered as an annual crop, thereby differing from most of the other varnish resins. The annual gathering takes place about the end of March, the bark being extensively cut and slashed, and the gum which flows from these incisions being afterwards collected. This resin hardens rapidly. The supply has been steadily decreasing and the cost, in consequence, rapidly increasing, so that Sierra Leone is not now used to a very great extent in the United States.

Two samples were examined with the following results:

Number.	Description.	Before oxidation.		After oxidation.	
		Acid.	Iodine.	Acid.	Iodine.
1.....	Finest select No. 1	118	105	116	105
2.....	No. 2 grade	114	102	116	108

It therefore appears that Sierra Leone is not readily oxidized. Hot saponification showed absence of esters.

BRAZILIAN COPAL.

Brazilian copal is a semi-fossil resin of uncertain botanical source from South America. Three samples were examined with the following results:

Number.	Description.	Before oxidation.		After oxidation.	
		Acid.	Iodine.	Acid.	Iodine.
1.....	Fine "bold" yellow	131	123	138	116
2.....	" " white	143	134	150	119
3.....	" " "	149	125	158	116

DAMAR.

While Damar is neither a fossil nor semi-fossil resin, and hence not strictly included under the title of this paper, its importance in varnish-making is such that it seems well to include it in consideration. The white damars used in the manufacture of varnish are commercially of three varieties—the Batavian from Java, and the Singapore and Padang from Sumatra. They are all exudations of *Dammara Orientalis,* the trees being cut periodically for the gum.

Eleven samples of white dammar were examined with the following results:

Number.	Description.	Acid.	Iodine.
1	Select Padang	24	116
2	" Singapore	55	104
3	" Batavian	24	124
4	No. 1 "	24	117
5	" 2 "	41	116
6	" 2 "	41	115
7	Batavian siftings	50	108
8	" "	50	107
9	" dust	51	104
10	" "	47	106
11	" "	50	103

The acid numbers were determined just as for all the preceding resins, using the same solvents. The decrease in the iodine absorption as the acid number increases shows that oxidation occurs with damar just as with the other resins. Hot, open saponification gives too high acid numbers for the same reason. Had Dieterich determined the iodine numbers of the damar dusts whose acid numbers he found high, he probably would not have concluded that the dusts were adulterated with colophony.

It would seem to the author that, in view of the results obtained, the value of the iodine absorption method as applied to the varnish resins is fully established. The almost universal tendency of the resins to oxidation when in contact with the air, as also brought out by this work, and the consequent wide range in acid and iodine values, makes it evident that chemical comparison of different samples of any resin are of value only when the samples to be compared are of the same general nature—in other words, it will not do to compare "bold" gum with "chips," or "Nubs" with "dust," for the reason that the finer the particles of gum, the farther the oxidation has progressed. But when it is desired, for the sake of greater accuracy, to supplement physical tests or inspection by chemical analysis, the author has found the following scheme of analysis accurate and reliable, *provided* it is used comparatively, that is, to test "dust" against "dust," "chips" against "chips," etc.

Moisture.—The resin is finely powdered and 1 gram dried for one hour at 110° C. on a watch crystal.

Insoluble Matter.—Two grams of the finely powdered resin are weighed out into a small beaker, and 25 cc. benzene and 10 cc. acetone added. Solution is complete for the softer resins in a few minutes, and slow for Zanzibar and the other harder resins. When necessary, solution of the latter may be effected in epichlorhydrin, aniline, or other more active solvent. When the solution is complete, allow to settle until clear, and decant the clear liquid, but *not* through the filter as it would clog the paper. Add more of the solvents to the residue in the beaker, and wash onto a filter-paper, previously washed out, the same solvents dried and weighed. Wash the residue clean, dry and weigh as total insoluble matter.

Ash.—Ignite paper and contents until white, and weigh residue as ash.

Insoluble Organic Matter.—The difference between the total insoluble matter and the ash represents the insoluble organic matter—bark and vegetable débris.

Indirect Acid Number.—Weigh out 1 gram of the finely powdered resin into a glass-stoppered bottle, add 15 cc. benzene, 5 cc. alcohol and 15 cc. fifth-normal alcoholic caustic potash. Allow to stand tightly stoppered for eighteen hours, add 25 cc. alcohol, a few drops phenolphthaleïn, and titrate back with fifth-normal

sulphuric acid. The number of milligrams of potassium hydroxide used represents the acid number.

Iodine Absorption.—Weigh out 0.2 gram of the finely powdered resin into a glass-stoppered bottle and add 10 cc. chloroform. Add 40-50 cc. of Hübl's iodine solution, allow to stand eighteen hours, then titrate back with thiosulphate.

Color.—Dissolve 10 grams of the resin in 100 cc. of a mixture of half benzene and half acetone, allow to stand in a 4-ounce oil vial until it has settled bright, then compare the colors of the clear solutions.

The above methods, when applied to the comparison of similar grades of the same resin, give surprisingly accurate results. Other things being equal, a higher percentage of insoluble organic matter, which would char in the kettle and darken the melt, or a higher acid number and lower iodine value, which would show more complete oxidation and hence indicate a more porous structure in the resin, or a darker color in solution, indicating a corresponding darker color when melted—these are the points which condemn a sample.

In conclusion, the author would state that he hopes soon to extend this investigation to the melted copals—especially to study the oxidation of the same, which may have important bearing on the durability of varnishes made from these resins.

CHICAGO VARNISH CO.,
CHICAGO, March, 1903.

ON THE RELATION OF THE SPECIFIC GRAVITY OF URINE TO THE SOLIDS PRESENT. SECOND PAPER.

BY J. H. LONG.

Received June 18, 1903.

SOME months ago[1] I gave the results of experiments carried out on the determination of the relation between the total solids of urine and the specific gravity at 25° C. A factor was found here corresponding to the coefficient of Haeser, but considerably larger than the number usually given, on account of the higher temperature at which the specific gravities were observed.

It seemed desirable to separate the effect of sodium chloride in fixing this relation, inasmuch as this substance is not a product

[1] This Journal, **25**, 257.

of metabolism and is present in extremely variable amounts which have no relation to the urinary constituents of true metabolic origin. A new set of tests were therefore made in which the chlorine was accurately determined and calculated to sodium chloride. Then the specific gravities of correspondingly weak chloride solutions were found and these were subtracted from the observed specific gravities at 25° to find the specific gravity due to metabolic products. There are, of course, slight sources of error in this calculation, but they are not of great importance in the final result. In the first place, the chlorine is not always present as sodium chloride; sometimes there is more chlorine than the sodium will combine with, but the excess is never great. Secondly, the specific gravity of a mixed solution is not accurately equal to the sum of the factors for each component taken separately. The excess of the specific gravity over unity for the mixed solution is not exactly the sum of the excesses for solutions of the component substances taken separately in the same volume. But for the dilute solutions considered here the variations are not of material importance, and besides, this whole calculation is an arbitrary one which cannot lead to more than approximate results.

The determinations were made as described in the former paper and the coefficient or factor C was calculated by the expression

$$C = \frac{\text{Solids} - \text{NaCl}}{E_{\text{total}} - E_{\text{NaCl}}},$$

in which E_{total} represents the excess of the specific gravity of the urine over 1, and E_{NaCl} represents the excess of the specific gravity of salt solutions of the strength found over 1. The results obtained are given in the table.

No.	Solids per liter.	Sodium chloride per liter.	Specific gravity $\frac{25°}{4°}$.	Sp. gr. of sodium chloride solution.	Coefficient for total solids.	Coefficient for solids less salt.
1	70.83	16.07	1.0287	1.0079	0.247	0.263
2	40.88	13.77	1.0169	1.0063	0.239	0.251
3	60.35	10.26	1.0233	1.0040	0.255	0.259
4	52.99	12.47	1.0190	1.0054	0.278	0.298
5	43.87	15.72	1.0184	1.0077	0.238	0.263
6	50.58	18.43	1.0216	1.0097	0.233	0.270
7	50.69	16.91	1.0217	1.0085	0.234	0.256
8	67.13	15.25	1.0275	1.0072	0.244	0.256
9	29.68	15.04	1.0131	1.0071	0.226	0.244
10	50.69	13.99	1.0217	1.0064	0.233	0.240
11	34.34	11.48	1.0130	1.0048	0.264	0.278
12	58.72	16.63	1.0234	1.0084	0.251	0.280

No.	Solids per liter.	Sodium chloride per liter.	Specific gravity $\frac{25°}{4°}$.	Sp. gr. of sodium chloride solution.	Coefficient for total solids.	Coefficient for solids less salt.
13	63.79	13.87	1.0238	1.0065	0.267	0.288
14	65.43	15.51	1.0260	1.0076	0.251	0.271
15	56.77	13.65	1.0234	1.0062	0.243	0.251
16	61.50	15.19	1.0238	1.0072	0.259	0.278
17	44.34	13.56	1.0172	1.0062	0.258	0.280
18	51.52	17.64	1.0202	1.0092	0.255	0.308
19	59.96	18.97	1.0235	1.0102	0.255	0.306
20	40.09	11.55	1.0154	1.0048	0.263	0.269
21	58.92	15.13	1.0230	1.0071	0.256	0.275
22	52.18	14.64	1.0213	1.0069	0.245	0.261
23	52.99	10.25	1.0190	1.0040	0.278	0.285
24	55.03	15.24	1.0220	1.0073	0.250	0.257
Mean,	53.05	14.63	1.0211	1.0069	0.251	0.271

It will be observed that the coefficient for the total solids is 0.251 and slightly smaller than the mean value found before, 0.260. The coefficient for solids, less sodium chloride, is considerably larger and, contrary to expectations, is the mean of results which show wider variations than in the other case. Most of the individual results are, however, near the mean value and for certain classes of calculations, therefore, the coefficient may be used with only a small probable error. It will be noted that the urines tested showed a range of concentration between about 30 and 70 grams per liter of solids.

NORTHWESTERN UNIVERSITY,
CHICAGO, JUNE, 1903.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 69.]

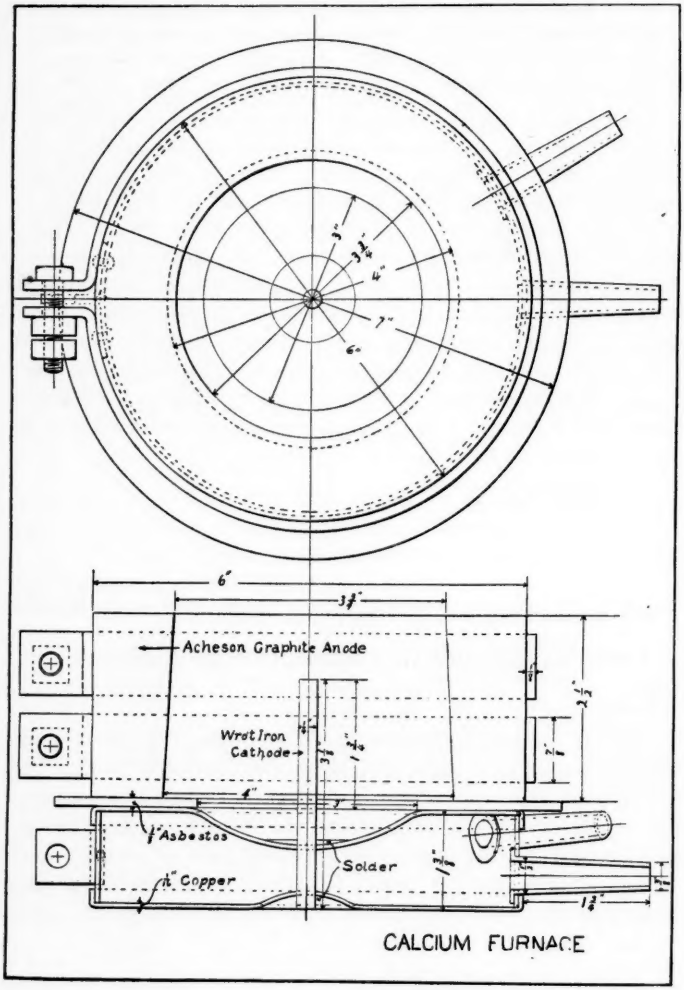
THE ELECTROLYTIC PRODUCTION OF CALCIUM.

BY JOSEPH H. GOODWIN.

Received June 26, 1903.

SEVERAL suggestions have been offered during the past year for the preparation of metallic calcium in the electrolytic way. The attempts made by the writer, with various furnaces, were fruitless. After much experimentation, the furnace, pictured below, was devised, and as it gave an excellent yield of metal it was thought that perhaps it would be helpful to others, hence this communication. Its construction is evident from the sketch. The

cathode of wrought iron is firmly fastened in electrical contact with a copper water-jacket, which serves as a cooler and as base for the furnace. Separated from this base by asbestos is a ring of graphite, made by boring out a 2.5-inch disk from a 6-inch Acheson graphite electrode. This ring constitutes the walls of the furnace and is also the anode, its electric connection being made by two wrought iron bands clamped firmly about it.



When the furnace has been arranged, spread powdered lime to the depth of half an inch over the bottom, pressing it down until it forms a firm, smooth floor. A stream of water is then sent through the jacket and the switch closed. Anhydrous calcium chloride, fused for half an hour in a wind furnace, is next poured into the furnace. It does not readily "wet" the graphite, it shrinks away from it; consequently a sheet of beautiful purple light separates the chloride from the graphite. It is an electric arc with a back electromotive force of 50 volts, which lowers the current. Contact between the chloride and graphite can be made by immersing a carbon rod along side the anode or by splashing the electrolyte against the graphite ring. The resistance should be cut out until a current of 100 amperes is passing. There will be a copious evolution of chlorine, for the removal of which a good "hood" is essential. Calcium chloride should be poured in from time to time, the temperature of the cell being kept at 950°. The liberated calcium melts from the iron rod upon which it has been deposited and floats to the surface, forming there a globule which, when about an inch in diameter, is removed with a small sheet-iron spoon.

The purity of the metal obtained in this manner varies with the purity of the chloride. Specimens made from chloride gotten from ordinary calcite showed, on analysis:

	Per cent.
Ca	94.80
Mg	4.16
Fe	1.03
	99.99

The metal calcium is rather brittle. On a fractured surface it is more brilliant than steel, with a gray-white color. When cut or filed, it exhibits a yellow tinge, resembling German silver or gold alloyed with a great excess of silver. Globules of metal may be freed from chloride with alcohol and then ground on an emery wheel, when they become very bright. If preserved under petroleum, their metallic luster is retained.

Metallic calcium is quite stable. The red-hot, molten metal can be stirred about in the furnace quite vigorously, and even be dipped out and poured back without igniting. If, however, some of the metal be collected on a wire and struck smartly on the table, it will fly in all directions with a hissing sound and burn violently

with a blinding light. Similar energetic action takes place when the hot metal comes in contact with asbestos or with other reducible substances.

The attempts to prepare strontium were not very successful. It is quite probable that the furnace will have to be somewhat modified for this purpose and also for the isolation of barium.

UNIVERSITY OF PENNSYLVANIA.

NOTES.

The Preparation of Oxygen.—The action of dilute sulphuric acid on potassium permanganate affords a satisfactory method of making oxygen in small quantities. The possibilities are well known, but do not appear to have been utilized to that end except in connection with hydrogen peroxide.

The operation consists in heating gently a mixture of potassium permanganate and an excess of dilute sulphuric acid, in a generating flask provided with safety and delivery tubes. As this mixture begins to give off oxygen freely at 50°, very little heat is needed. The evolution of gas is continuous and quiet and under easy control.

The amount of oxygen to be obtained by this reaction is approximately represented by the equation

$$2KMnO_4 + H_2SO_4 = K_2SO_4 + 2MnO_2 + H_2O + 3O.$$

Ten grams of potassium permanganate (treated with 40-50 cc. of 1:4 sulphuric acid) give somewhat more than a liter of oxygen.

Convenient and safe, this method may be used to advantage in making oxygen for experimental purposes in courses in general chemistry. R. B. RIGGS.

Note on the Effect of Combined Carbon in Iron on the Test for Tin.—A common test for tin depends on the reducing action of stannous chloride on mercuric chloride. If iron be used to reduce the tin, it should not contain any considerable amount of combined carbon, otherwise a counterfeit test may be obtained, no tin being present.

On making blank tests, it was found that, when the iron contained as much as 0.2 per cent. of combined carbon, its hydro-

chloric acid solution gave, with mercuric chloride, a very perceptible cloudy appearance in a few seconds. Some of the iron solutions yielded heavy precipitates at once.

The unsaturated hydrocarbons, liberated by the action of the acid on the iron carbides, seem to be the cause of this precipitation, and it is, roughly estimated, proportional to their odor. This odor is moreover destroyed by an excess of mercuric chloride, and further, if the solutions be previously heated until odorless, there is no precipitation.

Whatever be the cause, the action here is one of reduction and the precipitate formed is essentially mercurous chloride. Made in quantity, it was a dense, pure white, crystalline substance. When volatilized, a slight black residue generally remained. 0.8592 gram material gave 0.27 per cent. C. The action of such reagents as ammonium and potassium hydroxide, iodine and potassium iodide left no doubt as to its essential character, and a chlorine determination gave 14.93 per cent.; theory, 15.04 per cent.

In conclusion it may be said that, if the iron gives more than a faint "hydrocarbon odor" with hydrochloric acid, its solution will give a precipitate with mercuric chloride, and so interfere with the test for tin. Common wire nails may generally be used. Although their solutions have a reducing action, it is usually very slight and requires some time to develop sufficiently to be recognized.

R. B. Riggs and E. S. Merriam.

NEW BOOKS.

The Chemistry of Pigments. By Ernest J. Parry and John H. Coste. First edition, 1903. London: Scott, Greenwood & Co. New York: D. Van Nostrand Co. 275 pages, illustrated. Price, $4.50 net.

This volume treats of the chemistry of pigments used for protective, decorative and artistic purposes. A brief introduction describes in a popular way the elements of the science of color, the spectrum and absorption spectra. In the second chapter are discussed the uses of pigments, the forms and combinations in which they are applied, and the mal-influence of air, moisture and gases on the paints. A number of tests are given that show the comparative resistance of the various paint-skins to these

agents, but there is no mention of the important precautions in applying the paint, etc., whose neglect so often results in unsatisfactory or contradictory deductions.

The following section deals with the inorganic pigments. Some eighteen pages are devoted to white lead and its manufacture. The authors adopt the theory of a chemical combination between white lead and linseed oil, a point that has been disputed by several investigators. The iron oxides, lead, chrome and copper compounds, and the carbon pigments are described in turn. Under the head of organic pigments are Prussian blue and the lakes of carmine, Brazilwood, and other animal and vegetable colors, and a number of the coal-tar dyes. An account of indigo and some minor organic pigments closes the volume.

The work can be commended for what it essays, to both the general reader and the chemist whose work is mainly in other departments. The space allotted to the description of the various pigments appears, on the whole, to be fairly well distributed, though the paragraphs on the vermillionettes, red lead and asphalt could have been amplified with advantage; on the other hand, the methods of chemical analysis of certain pigments might well have been omitted, since one competent to make such analyses always has access to detailed descriptions of the most recent and approved methods.

The book has a good index, and the print and binding are satisfactory. FRANK JULIAN.

THE PRINCIPLES OF LEATHER MANUFACTURE. By H. R. PROCTER, F.I.C., F.C.S. London: E. and F. N. Spon, Limited. New York: Spon and Chamberlain, 1903. xvi + 512 pp. Price, $7.50.

The well known "Text-Book of Tanning," by the same author, having been long out of print, it was desirable to issue a revised edition which, however, takes the form of two books. The present volume contains a very satisfactory discussion of the principles on which the manufacture of leather is based, details of working processes being in the main excluded. Analytical processes and operations of chemical control for the tannery are found in the volume already published as the "Leather Industries Laboratory Book," a work now well known to chemists. To complete the series, a third volume, dealing with manufacturing processes, is desired.

In view of our very limited knowledge of the nature of the changes involved in leather-making, the author specifically points out the value, to the tanner, of practical experience and acquaintance with his material. There is a large amount of very useful information to the practical tanner in these pages: The effect on the leather, of the early treatment of the hide, such as drying, salting, etc.; the causes of injury to hides; the action of hard water in washing and soaking hides, and extracting tannin; the causes of swelling by dilute acids or alkalies, and the shrinking action of strong solutions; the nature of the changes produced in bating, puering and drenching, and the properties of the various materials used, are some of the points which are fully discussed.

Chrome tannage receives about eighteen pages of largely theoretical discussion, but the intelligent tanner, who has a little chemical knowledge, can pick out of this brief summary many bits of valuable information. The importance of this branch of the industry would seem to justify a somewhat more extended consideration.

The occurrence and properties of the vegetable tanning materials are fully described. The chapters on the grinding and extracting of tanning materials, and their analysis, and the chemistry of their action, contain many valuable hints. The chapter on dyes and dyeing is very satisfactory, while that on the construction of tanneries will furnish useful data to architects and builders who may be called on for this kind of work. The oil tannages and the properties of fats, soaps, waxes, etc., are all well considered; also the important items of evaporation, heating and drying; the disposal of wastes closes the text proper. Official methods of tanning analysis, both European and American, and a list of coal-tar colors suitable for use on leather, constitute the three appendices. Frequent foot-note references to original papers throughout the text add greatly to the convenience and value of the book.

Numerous illustrations are scattered throughout the book and the plates are noticeably clear and sharp, but some of the half-tone pictures from photographs are unsatisfactory; a comparison between Figs. 28, 29 and 42*a*, with Figs. 31 and 32, *e.g.*, leaves much to be desired in the former cases. The reference to Fig.

29 on page 223 is evidently a misprint, and the paragraph is somewhat obscure. The typography and general make-up of the book is good. The literature of tanning has long needed such a work as this.

The importance of technical education for tanners is now generally recognized, and the appearance of this work by one who is an acknowledged authority and leader in this educational movement, will doubtless further elevate the technical school in the estimation of successful tanners. F. H. THORP.

THE PRAXIS OF URINARY ANALYSIS. A GUIDE TO THE CHEMICAL ANALYSIS OF URINE. BY DR. LASSAR-COHN. Authorized English translation by DR. H. W. F. LORENZ. New York : John Wiley and Sons. 1903. 58 pp. Price, $1.00.

This little book is printed on very heavy paper, almost cardboard thickness, and heavily leaded to increase apparent size. It contains a few of the simplest qualitative reactions employed by physicians in the analysis of urine and directions for three quantitative determinations. These are so meager, however, that they are of no practical use. In addition to the urine tests, a few pages are devoted to the analysis of stomach contents. The amount of practical information contained in the book is so small that it can not be recommended to students or practitioners of medicine. The English of the translation is not always good. J. H. LONG.

A TEXT-BOOK OF VOLUMETRIC ANALYSIS. With special reference to the volumetric processes of the pharmacopoeia of the United States. Designed for the use of pharmacists and pharmaceutical students. BY HENRY W. SCHIMPF, PH.G., M.D. New York : John Wiley and Sons. 1893. Fourth edition. 60 figures. 12mo. xxiii + 553 pp. Cloth. Price, $2.50.

As the title suggests, this work is intended exclusively for the use of pharmacists, and its appearance in a fourth edition gives evidence that it meets a need of those for whom it is written to a greater degree, in some respects, at least, than any other available book. Its merit lies chiefly in the variety of methods offered, a direction in which most texts on the subject are deficient.

It is a collection of receipts for volumetric analysis and is almost wholly lacking in explanatory matter or in any exposition of the

reasons for doing things in one way rather than in another. The few explanations given are often inaccurate or positively incorrect. As an instance of this, the statement is made (p. 183) that sulphurous acid must be diluted to 0.04 per cent. before titrating it, "for if it is not sufficiently diluted there is risk of the sulphuric acid formed, being again reduced to sulphurous, with liberation of iodine, thus causing irregular results." This explanation has, of course, been exploded long ago. If true, it would mean that sulphuric acid of a dilution corresponding to 0.04 per cent. of sulphurous acid has an oxidizing action on potassium iodide and is reduced by it, a state of things which every chemist knows does not exist.

The directions are not always couched in the clear and pure English that one may properly expect to find in a text intended for student use; witness the following sentence taken at random from page 478. "Warm the mixture . . . . and add . . . . iodine solution from a burette until the brown color of the iodine solution is no longer decolorized and the mixture in the flask assumes a permanent, brownish yellow color, and upon shaking deposits a red-colored precipitate if much carbolic acid is present." Comment is unnecessary.

On the same page, the name of the well-known chemist Vortmann appears as "Wortmann," and the source of a paper which was published in the *Berichte* is given as "Pharm. Zeit. f. Russland." Perhaps it was Russian influence that changed the *V* to a *W*!

The method of titrating iodides by a mercuric chloride solution, due to Personne, is described without a word regarding the precautions which must be observed to obtain even tolerably correct results. The book shows throughout, with the exception of Chapter LXII relating to the determination of alkaloids, abundant evidence of being a compilation from other text-books rather than from original sources. The illustrations leave something to be desired, both as to execution and design. It seems to the reviewer scarcely necessary to introduce a cut of a liter-flask, unless some point regarding the model, etc., is to be elucidated. The picture of a liter-flask in the text bears the inscription "14.° R."!

LAUNCELOT W. ANDREWS.

ERRATA.

In the paper by Albert P. Sy on "A New Test for the Stability of Nitrocellulose Powders," the following corrections should be inserted:

On page 565, *for* Fig. 7, *read* Fig. 10.
" " 567, line 5, *for* Fig. 1 *read* Fig. 10.
" " 567, *for* Fig. 8 *read* Fig. 7.
" " 568, *for* Fig. 9 *read* Fig. 8.
" " 568, *for* Fig. 10 *read* Fig. 9.

VOL. XXV. [SEPTEMBER, 1903.] NO. 9.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 70.]

THE USE OF A MERCURY CATHODE IN ELECTROCHEMICAL ANALYSIS.

BY EDGAR F. SMITH.

Received June 26, 1903.

THE suggestion of precipitating metals in the form of amalgams was first made (1880) by Wolcott Gibbs,[1] who described a new scheme for the electrolytic determination of metals, before the National Academy of Sciences, in which scheme he recommended weighing out in a small beaker a definite amount of metallic mercury which was, by means of a platinum wire, connected with a battery and made the cathode, while in the salt solution, contained in the beaker, was suspended a strip of platinum, serving as the anode. The currents used varied greatly in strength. Salts of mercury, tin and cobalt were apparently decomposed, their respective metals being precipitated upon or in the mercury cathode. Quantitative results do not appear. The author of this method believed that possibly sodium and potassium might be separated in this manner and Professor Hunt remarked that the "process came with the beauty and force of a revelation."

[1] *Chem. News*, **42**, 291.